THE EXAMINATION OF
HYDROCARBON OILS
AND OF SAPONIFIABLE
FATS AND WAXES

BY

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FORMERLY, PRIVY COUNCILOR, AND SUBDIRECTOR, THE ROYAL BUREAU FOR TESTING MATERIALS OF BERLIN-LICHTERFELDE. DOCENT AT THE TECHNISCHE HOCHSCHULE, BERLIN

AUTHORIZED TRANSLATION FROM THE FIFTH GERMAN EDITION

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PREFACE TO THE FIFTH GERMAN EDITION

The fifth German edition was delayed in publication until the close of the Great War; this, however, made it possible to present in its pages many of the important developments in oil chemistry brought out by the exigencies of the times. Thus it has been possible to discuss the chemistry of the various materials which were used by the German nation during the stress of war as substitutes for linseed-oil varnish, for resins, for cutting oils, for soaps, and for lubricants in general. New sections on electrical tests and various electrical phenomena, on heat of fusion, on graphite lubrication, on surface tension, on cumarone resins, on artificial resins and on rosin size have been introduced. Other chapters, such as those on viscosity, on the theory of lubrication, on calorimetric determinations, on turpentine and its substitutes, on wool grease, on cholesterin, and on soaps, have been reconstructed.

In spite of simplification of text, tables and general arrangement of material, the new edition contains nearly 200 more pages, 19 more figures and 30 more tables than the fourth German edition.

Each section of analytical procedure has again been preceded by a discussion of the industrial importance and technical use of the material in question, thus making the book, it is hoped, much more than a series of cook-book recipes. Many first class handbooks are available for a more detailed study of the individual subjects but the author has felt it inadvisable to omit or to shorten such theoretical or technical discussions. It is often impossible to interpret properly the results of an analysis unless such general information concerning the intended use of the material is at the command of the analyst. Of course for a more detailed and more exact discussion of these general matters it will be necessary to consult the handbooks of industrial chemistry and various monographs of the separate industries.

The special chapters dealing with the chemistry, technology and the analysis of the various groups of bodies (such as petroleum and petroleum products, tars and tar-oil products, ozocerite, saponifiable fats and waxes) have in this edition been preceded by a section devoted to the general physical, physico-chemical and chemical tests which it has been found useful to customarily apply to all materials covered by

the general term "Hydrocarbon Oils and Saponifiable Fats and Waxes." *In this general section there have been introduced many discussions of importance in the industrial application of these methods.*

The author has received many valuable suggestions from a host of distinguished colleagues. In particular does he wish to acknowledge the helpful efforts of Dr. G. Meyerheim in revising and correcting the manuscript. Various sections have been carefully read and revised by specialists in their branch of the industry. The author most heartily thanks his friends for their many suggestions and for their helpful criticism.

BERLIN-WILMERSDORF HOLDE

PREFACE TO THE FOURTH EDITION

The change of title from "Mineral Oils" of the preceding editions to that of "Hydrocarbon Oils" of the present fourth edition seemed necessary for several reasons. The term "Mineral Oils" includes in a narrow sense only petroleum products but in a somewhat wider sense may include lignite-tar oils and shale oils. There is, however, some doubt whether the coal-tar oils, discussed even more fully than in previous editions, could be called mineral oils. Moreover the previously included light and heavy rosin oils, turpentine oils and pine oils certainly cannot be classified as mineral oils.

Since the appearance of the third edition in November, 1909, important work concerning gas oils, oils for Diesel motors, the theory of lubrication, etc., has been published and this, together with the newer specifications for gas oils, Diesel motor oils, etc., resulting from the work of Spiegel, Hempel and Rieppel, had to be considered in connection with many other specifications. Furthermore all the newer recognized contributions of theoretical interest or analytical value have been carefully gone over. There have been added new sections on the determination of fuel value, on the physiological properties of petroleum products, on the nomenclature of bitumens, etc. Numerous tables of physical constants have been introduced to avoid as much as possible the necessity of reference to other books. The chapters on coal tar, asphalt and its substitutes, ozokerite and several chapters on the fat industry, notably on hardening of oils, glycerine, varnish, etc., have been enlarged.

In general, in order to avoid uncertainty in the mind of the analyst, it has been the aim to describe only such methods as have been found useful in, or have been tested by, the Royal Bureau of Testing Materials, or such processes as may be considered trustworthy through the experience of others. The book can therefore not be considered as a complete compilation of the immense literature on the subject; for details the reader is referred to the various handbooks which have recently appeared.

An attempt has been made to restrict the size of the book by eliminating unnecessary text, by reducing the size of cuts, and by omitting

many details which did not seem absolutely necessary for a clear presentation.

In the preparation of the new edition, the author has received the enthusiastic assistance of Dr. G. Meyerheim with whom he has been associated for some years at the Royal Bureau for Testing Materials.

The author also wishes to acknowledge his indebtedness for the many kindly and helpful suggestions offered by colleagues working in various scientific and industrial fields.

BERLIN, LICHTERFELDE HOLDE

TRANSLATOR'S PREFACE

TO THE

SECOND ENGLISH EDITION

The rapidity with which the successive German editions of Professor Holde's "Hydrocarbon Oils and Saponifiable Fats and Waxes" have appeared points to a widespread demand among German chemists for a book on these subjects. It is hoped that this translation will make available for English-speaking chemists many useful methods in addition to those common in industrial practice here.

It is believed that the wide range of topics covered from a common standpoint renders the book unique in its availability for general work. The very complete treatment in one compact volume of general methods of oil analysis, petroleum and petroleum products, lubricants, natural asphalt, ozocerite, tars from various bituminous materials, together with saponifiable fats, industrial products prepared from them, and waxes, should render the book extremely useful in laboratory investigations.

It may at first glance appear too presumptuous an effort to attempt adequate treatment of saponifiable fats and oils and so wide a range of their industrial products in two chapters of 200 pages, but by free use of tabular statements of properties, reactions and data, the author has succeeded in collecting in so small a space an immense amount of material in a very handy form for reference. Constants for many new raw materials are presented in tabular form for the first time.

Over 200 pages are devoted to petroleum and petroleum products; this discussion, amplified by an extensive resort to tabulation of physical properties, chemical reactions and industrial data, has made available for our petroleum chemists the procedures favored by the continental laboratories. It is this compendium of first-hand knowledge concerning petroleum chemistry which has brought for Dr. Holde's book the favorable reception and praise of German chemists.

The more than 70 pages devoted to lubrication will be read with profit by all lubrication experts who may wish to learn of European practice.

This new English edition based on the fifth German edition is

practically rewritten; hardly a page remains the same as in the first English edition. As the fifth German edition appeared in a form containing nearly 200 more pages than the fourth edition, it seemed necessary to offer the English translation with a somewhat larger page and with a greater proportion of the analytical procedures in smaller type; this has made it possible, without important omissions, to restrict the increase in the size of the book to something over 100 pages. Thus it is still possible for the oil chemist to have available in one volume a comprehensive treatment from a common standpoint of all the more usual materials considered by the industrial specialist in oils.

As pointed out in the author's preface many completely new sections on special oils have been introduced, and practically all chapters have undergone fundamental and extensive revision. The introduction of a special chapter on general methods of analysis (dealing with such subjects as specific gravity, viscosity, surface tension, heat measurement, electrical tests, optical examination, flash point and melting point determinations and coefficient of expansion as well as such general chemical tests as those for acidity, water content, mechanical impurities, ash, glue, saponifiable and unsaponifiable oil) has made possible the shortening of some of the special chapters and thus allowed the introduction of more technical material concerning the various industrial products.

The reader will perhaps be interested in the many revelations made concerning the straits to which the German oil industry was brought by the lack of raw material during the war and it may show how effective the blockade became towards the end. There can be little doubt that the general lowering of standards and the resort to makeshifts such as are disclosed in the text helped to bring the war to a successful conclusion.

In attempting to make the translation as useful as possible, some minor rearrangements and omissions have been necessary, but it is hoped that nothing essential to a clear understanding has been omitted.

Considerable attention has been directed to the preparation of an adequate index.

EDWARD MUELLER

CAMBRIDGE, MASS.
June, 1922.

CONTENTS

CHAPTER I

GENERAL METHODS OF EXAMINATION

CHAPTER III

NATURAL ASPHALT

CHAPTER IV

OZOCERITE (EARTH WAX)

CHAPTER V

HYDROCARBONS (TARS) OBTAINED BY DISTILLATION OF COAL, SHALE, RESINS AND WOOD

CHAPTER VI

VEGETABLE AND ANIMAL FATS AND OILS

CHAPTER VII

INDUSTRIAL PRODUCTS PREPARED FROM FATS

CHAPTER VIII

WAXES

CHAPTER IX

PHYSICO-CHEMICAL TABLES

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HYDROCARBON OILS AND SAPONIFIABLE FATS AND WAXES

CHAPTER I

GENERAL METHODS OF EXAMINATION

A. Physical and Physico-chemical Tests

I. Specific Gravity

The specific gravity is used for the classification of pure petroleum products of known source, and also for the rapid comparison of many similar samples. In connection with other properties, it serves as a constant in the identification of certain oils and in the examination of oils for impurities (see Table 1).

Since water must be considered as an impurity in an oil, the specific gravity of dry samples only should be determined. If the oil contains no naphtha, it may be freed from water by prolonged warming and then decanting the oil from the water which may settle; or it may be dried by agitation with calcium chloride and then filtered. In the case of oils containing naphtha, only the latter method of treatment at room temperature is applicable.

TABLE 1

Specific Gravities of Various Oils at 15°

Russian kerosene	0.800–0.830
American kerosene	0.780–0.800
Russian paraffin oils, spindle oils, etc.	0.850–0.900
American paraffin oils, spindle oils, etc.	0.840–0.907
Russian machine oils	0.900–0 915
American machine oils (Texas up to 0.940)	0 875–0.914
Russian cylinder oils	0 909–0.932
American cylinder oils	0 883–0 895
Heavy rosin oils (with much rosin, to 1.0)	0 973–0.982
Coal-tar oils	1.090–1.100
Brown-coal tar oils	0.893–0.974
Non-drying vegetable oils	0.913–0.925
Semi-drying oils	0.921–0 936
Drying vegetable oils	0.923–0 943
Neat's-foot and bone oils	0.913–0.917
Liquid waxes (for example, sperm oil)	0.876–0.884

Cod liver oil	0.922–0.931
Whale oil	0.919–0.930
Porpoise oil	0.926–0.938
Seal oil	0.915–0.930
Turpentine oil	0.865–0.875
Naphtha	0.640–0.720
Pine oil	0.865–0.875
Turpentine substitutes	0.720–0.810

(*a*) The specific gravity can be rapidly determined by the hydrometer method which, however, is not very accurate, especially with the more viscous oils. Standardized hydrometers, with thermometer inclosed, can be obtained. These may be used for liquid fats and waxes, as well as mineral oils, if sufficient material is available. The values are recalculated to 15° C. (in some cases 20°) being referred to water at 4° C. as unity.

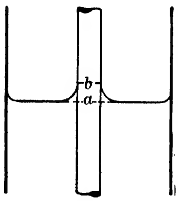


FIG. 1.

The glass cylinder, in which the oil is placed, should rest on a level support. The hydrometer is allowed to slowly sink into the oil. After 15 minutes the temperature of the oil is noted and the height of the meniscus on the freely moving spindle is observed (at *a*, Fig. 1). If the oil is very dark, the reading at the top of the meniscus (at *b*) is taken, and a correction of 0.0015 of 0.0010 added, depending on whether the diameter of the spindle is smaller or larger than 16 mm.

The values are recalculated to 15° C.; for every degree difference in the temperature, a correction, of ± 0.00068 for mineral lubricating oils, is made. In general the correction for an oil is the product of the specific gravity and the coefficient of expansion. For the values of the corrections for naphtha, kerosene, fatty oils, etc., see pages 116. 133, and 173.

Example:

Observed specific gravity	0.9010 at 17.5°
Correction for meniscus	0.0010
Temperature correction (0.00068) (2.5)	0.0017
Specific gravity at normal temperature	0.9037 at 15°

(*b*) If only small amounts of material are available and an accuracy to the third decimal place is sufficient, there can be used the sets of small hydrometers (16 cm. long) which have a range of from 0.640 to 0.940. These are not provided with thermometers in their stems, so that the temperature of the oil must be determined separately.

(*c*) **Pycnometer.** With small amounts of oil and with very thick cylinder oils and for more exact determinations in which the specific gravity is to be de-

termined to the fourth decimal place with an error of not more than 0.0004, the pycnometer of Göckel is used (Fig. 2); this contains exactly 10 c.c. at 15°. These pycnometers, if properly made, save much calculation since the specific gravity is obtained by division of the absolute weight of the oil filling by ten.

1. When more than 10 grams of oil are available: The weight of the pycnometer is determined filled with air (subtract 12 milligrams for the air contained). Then determine the weight filled with distilled water at a definite temperature (see page 535), calculate the weight at 4° and thus determine the volume of the pycnometer. For determining the specific gravity of the oil, the clean dry vessel is filled and kept at room temperature in a water bath for one-half to one hour till the temperature is constant, the vertical tube being kept full by dropping in oil; it is then taken by the neck, the excess of oil removed from the capillary, the glass cap put on, washed with benzol, wiped with a linen cloth, dried, then weighed and the specific gravity at 15° calculated.

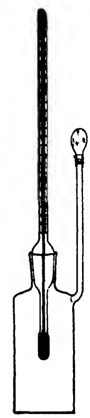


FIG. 2.

Viscous or salve-like oils which do not flow easily below 25° are warmed before pouring into the pycnometer and then kept in a water bath at 22 to 25° at constant temperature. Or the method of mixtures (with benzol) at room temperature may be used.

If the temperature during the determination of the specific gravity is higher than 30° a correction must be made for the change in volume of the pycnometer. The volume v of the pycnometer at the temperature t_2° is

$$v = \frac{m}{s}[1 + \alpha(t_2 - t_1)]$$

where m is mass, s is specific gravity of the water which fills the vessel at t_1° and α is the cubical coefficient of expansion of glass (0.000025).

If air bubbles form on filling, they are allowed to collect on the surface and are then removed by bringing the end of a glass rod near them; if in viscous oils the air bubbles do not rise easily, the oil is put in a drying oven at 50° and then, after removal of the bubbles, cooled to the desired temperature, more substance being added if necessary.

2. With very small amounts of oil which are not enough to fill small pycnometers, the pycnometer can still be used if it is filled almost up to the neck with water, then weighed, then filled with oil, and the thermometer so introduced that no water enters the neck or the tube. After cleaning it is again weighed. Water and oil are kept at constant temperature. If the amount of water in the vessel is subtracted from the water value of the pycnometer full, the volume w displaced by the weight of oil O is found. Then O/w will give the specific gravity of the oil. The results are recalculated to 15°.

Instead of using the water-difference method, the oil may be mixed with an equal volume of benzol and the specific gravity of the mixture at 15° determined. Then $D = 2M - N$ when D is the specific gravity of the oil, M that of the mixture and N that of the benzol.

With coal-tar oils, petroleum pitch, etc., which are heavier than water, a small amount of the material is poured onto the bottom of the vessel (melting if necessary), weighed, the vessel filled with water and then again weighed on drying.

(*d*) The alcohol flotation method may be used if very small amounts of oil insoluble in alcohol (for example, mineral lubricating oil and fatty oils but not castor oil or petroleum containing naphtha or kerosene) or solid fats or waxes (like tallow or spermaceti) are available.

Alcohol solutions of different specific gravities are tried to see in which the oil or melted fat sinks and rises. In this way the limits are determined within which the specific gravity lies. To the solution with the specific gravity nearest that of the oil, either water or alcohol is added with stirring until the oil drop neither rises nor falls. The specific gravity of the alcohol solution is then determined by one of the customary methods. Air bubbles in the oil and in the alcohol are to be avoided.

(*e*) **High-temperature Determination.** If the specific gravity of vaseline-like or even more solid lubricants is to be determined at high temperatures (say 100°) the Sprengel pycnometer (Fig. 3) or the Westphal balance with a special sinker and thermometer reading at 105° is used (Fig. 4). This method is applicable to bodies which remain homogeneous on warming (for example, paraffin, ceresine, wax).

1. **The Sprengel Pycnometer.** (Fig. 3.) This is filled with water to the mark and then weighed after closing with two glass stoppers. From the weight of the water at the temperature of the experiment the volume at 4° can be calculated. The dried pycnometer is filled by sucking the melted fat through *b* and is then heated in a water bath until no more expansion takes place; then so much is removed at *a* till the oil stands in *b* exactly at the mark *m*, the glass caps are put

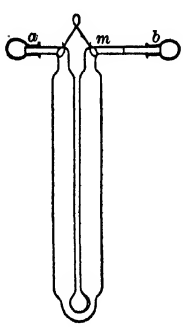


FIG. 3.

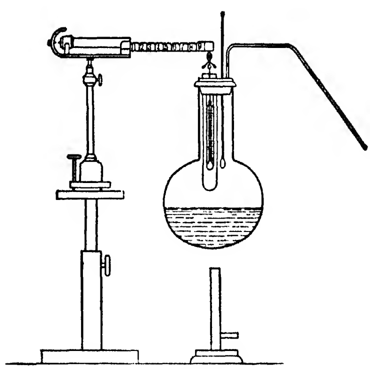


FIG. 4.

on and the tube is cooled and weighed after cleaning the exterior. In using this method a correction must be made for the change in the volume of the pycnometer in changing from room temperature to 100° C. By dividing the weight of the oil (necessary to fill the pycnometer at 100°) by the volume of the vessel at 100° the specific gravity is obtained.

2. Fig. 4 shows how the specific gravity of a fat heated to from 98 to 100° in a water bath in a (2 cm. diameter) test tube can be determined by the Westphal-Mohr balance. The balance is used in the customary manner.

(*f*) For the determination of the specific gravity at room temperature of materials (as greases), which do not remain homogeneous on melting, another method may be used.

The specific gravity of such salve-like and solid substances is determined at ordinary temperature by the method of Gintl (Fig. 5). The glass vessel closed at the bottom is 8 mm. in diameter and 20 mm. high; it is filled with the melted sample, allowing it to heap up over the top. Avoid inclosing air-bubbles. The glass cover has a ground-in groove. The pycnometer and cover are then fastened in the gilded clamp by means of the screw; the excess of substance squeezed out is wiped off with a piece of cloth dipped in naphtha.

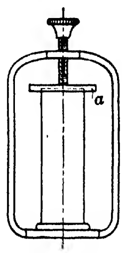


FIG. 5.

(*g*) For hard substances (pitch, asphalt) having a specific gravity greater than 1.

1. The weight (m) of a small amount of material is found; a small pycnometer of 10 c.c. capacity is weighed filled with water (p), and again after introducing the material (p_1). Then $p + m - p_1$ must be the weight of the water displaced by m, and

$$\frac{(m)\,(s_t)}{p + m - p_1}$$

will be the specific gravity of the asphalt at the temperature of the experiment, s_t being the density of water at this temperature.

2. A simple method for determining the specific gravity of asphalt, as well as of other substances contracting on solidification (paraffin, wax, etc.), has been devised by Sommer.*

It is a difficult matter to fill even a cylindrical vessel completely with a substance which contracts on solidification. To overcome this difficulty a riser (as in casting iron) is attached. After cooling the cast material in a constant-temperature bath, the excess is cut off with a warmed knife and the specific gravity is determined by weighing.

II. Coefficient of Expansion

This constant is required for the recalculation of the specific gravity to other temperatures and for calculating the expansion of an oil during storage and transport.† The coefficient of expansion is that fraction of unit volume by which one unit volume expands on being heated one degree.

* Graefe, Petrol., 5, 266 (1909).

† Holde, Mitteilungen, 11, 45 (1893); Singer, Chem. Rev., 3, 289 (1896).

The coefficient of expansion is either calculated from the specific gravities determined in the pycknometer at different temperatures (this works up to 30°), or directly determined in dilatometers.

(*a*) **The specific gravity method.** In this case the coefficient of expansion is calculated, if the specific gravities a and b are known for the temperatures t and t_1, as follows:

$$\alpha = \frac{a - b}{b(t_1 - t)}.$$

(*b*) **The dilatometer method.** The following method of Holde allows the direct determination for temperatures above 30° and allows the simultaneous testing of ten oils (Figs. 6 to 9).

The dilatometers (Fig. 6) have a capacity of about 30 c.c., with a neck 2 mm. in diameter and a capacity of 850 cubic millimeters. The original volume is taken

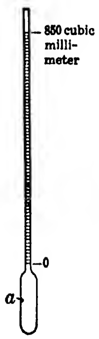


FIG. 6.

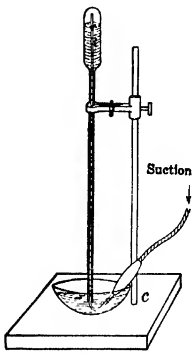


FIG. 7.

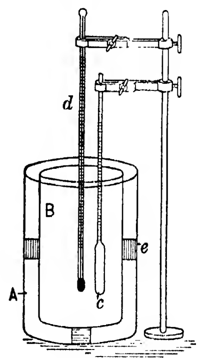


FIG. 8.

in a large water bath (Fig. 8); the final reading, in the arrangement shown in Fig. 9. The temperature in this latter arrangement can be kept constant by using various volatile substances as the liquid in A (see page 543). As many as ten dilatometers can be hung in B together with a standardized thermometer graduated to tenths of a degree. The dilatometers are filled by means of a copper or brass capillary (Fig. 7) and are emptied in a similar manner by blowing in air. Air bubbles in the oil clinging to the neck when the capillary is withdrawn can be removed by repeated gentle suction with the capillary. Oil clinging to the capillary above the level in the tube may be removed by a cotton swab on the end of a wire. The tubes are cleaned with ether; the ether is blown out with air. The neck must be calibrated before use by weighing either mercury or water or by measuring the length of a thread of mercury.* Correction tables must be prepared for each tube. The volume up to the zero mark is determined by weighing either water or oil, the weights being reduced to vacuum.

* Calibrated tubes can be obtained from Dr. Göckel, Berlin, Luisenstrasse 21.

The calculation is made by means of the formula

$$\alpha = \frac{V_1 - V}{(t_1 - t)V} + c,$$

where V is the original volume at the temperature t, V_1 is the volume at the higher temperature t_1 and c the coefficient of expansion of the glass (0.000025) which can be determined from the apparent expansion of mercury in the vessels.

With homogeneous liquid mineral oils the coefficient of expansion increases with the temperature similar to the behavior of other liquids; with oils containing suspended solid particles, α decreases until all the solid is melted. The value of the coefficient of expansion depends upon the material examined; in oils of similar character and common origin it will decrease with an increase in specific gravity (in Russian oils it ranges from 0.000949 for petroleum ether to 0.000632 for lubricating oil). For mineral lubricating oils the values range from 0.00063 to 0.00081; for fatty oils, from 0.000654 to 0.000838.

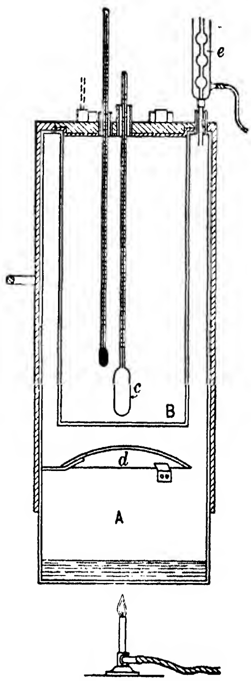


FIG. 9.

III. VISCOSITY

The viscosity is of great importance in the commercial valuation of oils. As a measure of internal friction, the viscosity serves as a criterion of the usefulness of lubricating oils for certain purposes (see theory of lubrication, page 167); in the case of illuminating oil, the ability to rise in the wick is dependent upon the degree of fluidity; in the flow of oils through pipes, the viscosity is important in determining the size of the pipes, and in determining the pressure to be applied; in the case of fatty oils, which have not been altered by prolonged storage, the viscosity is a characteristic constant.

(a) Determination by means of capillaries

1. Theory

The absolute internal friction is the force $[\eta]$, expressed in absolute units, necessary to move a layer of liquid of one square centimeter area over a layer of the same size and one centimeter distant, with a velocity of one centimeter per second.

This force is determined in the case of liquids by measuring the rate of flow through capillaries under a determined constant pressure; with very thick oils the falling weight method is used.

Use is made of the formula suggested by Poiseuille

$$[\eta] = \frac{(\pi)\,(p)\,(r)^4}{(8)\,(v)\,(l)}\,t,$$

where η is the absolute internal friction, p is the pressure in grams per square centimeter, r is the radius of the capillary, l is its length in centimeters, and v is the volume in cubic centimeters which passed out in the time t in seconds.

2. Apparatus (Fig. 11)

The oil in the capillary *odcp* is blown by air applied at o under constant (equivalent to a water column of 600 mm.) pressure by means of the arrangement AB through the capillary attached to cd (Fig. 10); the rate of flow is determined by noting the time necessary for the bulb e to fill from the mark d_1 to c_1. The result may be checked by attaching the rubber tube to p, and then driving the oil from the bulb e back into g, and noting the time required.

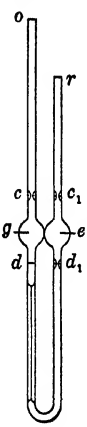


Fig. 10

(*a*) **Form of the capillary.** The tubes suggested by Ubbelohde (Fig. 10) avoid the deficiencies of the capillaries suggested by Ostwald and Traube. These tubes have the advantage of compensating for the effect of oils of different specific gravities upon the pressure, because the difference in level cd_1 at the beginning of the experiment is the same as c_1d at the end.

(*b*) **Calibration.** In the examination of oils of differing high viscosity, I. Traube* suggests the use of a series of capillaries, of which the narrower ones are directly calibrated with water at 0° C., by noting the time of efflux in the apparatus to be described; the wider capillaries, in which the time of outflow of water would be too short (less than 50 seconds), are calibrated by determining the length of time necessary for oils of higher viscosity to pass through the capillaries.

For example:

Calibration value of Tube I (time of outflow of water at 0°) 926.3 sec.
Calibration value of Tube II (time of outflow of water at 0°) 103.9 sec.
Calibration value of Tube III (time of outflow of water at 0°) 53.3 sec.

These values were directly determined with water. In calibrating Tube IV, an oil (*a*) was found to discharge from Tube III in 3946 seconds, but required only

* Zeitschrift des Vereins deutscher Ingenieure, 1885, 882.

593.5 seconds to flow from Tube IV. In calibrating Tube V, an oil (b) was found to discharge from Tube IV in 1249 seconds, but required 375 seconds to escape from Tube V. From these data may be calculated the calibration values of Tubes IV and V in terms of water. As follows: 3946 divided by 53.3 equals 74, this being the specific viscosity (η) of the oil (a) referred to water at 0° as unity; then dividing 593.5 (time of efflux from Tube IV) by 74, we get 8.0 as the calibration value of Tube III in terms of water. Similarly, 1249 divided by 8.0 equals 156.0, this being the specific viscosity (η) of the oil (b) referred to water at 0° as unity; dividing 375 (time of efflux from Tube V) by 156, we get 2.4 as the calibration value of Tube V.

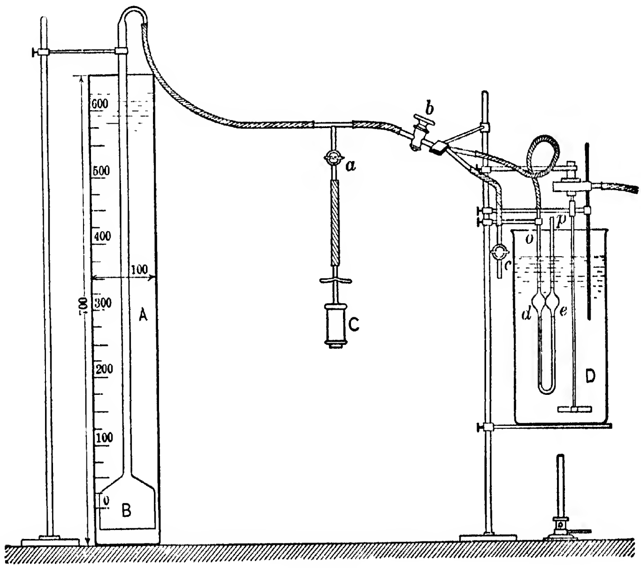


FIG. 11.

(c) **Pressure apparatus.** At the beginning of a run, with cock a open and with cock b closed, the water pressure in the reversed Buchner funnel B is adjusted to 600 mm. by means of the hand-bellows C. The cock a is then closed.

(d) To fill the capillary, the end o is dipped into a dish containing some of the oil; by then applying suction at p, the tube will be filled to the bend. The tube is then attached by rubber tubing to the T-tube with the closed cocks, b and c. It is placed in the water bath D, together with a thermometer and stirrer, and allowed to come to the temperature of the experiment. Dark oils, or light-colored oils containing gross impurities, are filtered through a sieve before the experiment.

(e) The time of outflow is taken by noting the exact number of seconds necessary for the passage of the oil from the position d_1 to c_1. After noting the time, the cock b is closed, c is opened, the rubber tube attached to the end of p, c is closed, the pressure adjusted to 600 mm., b is opened, and then the time necessary for the oil to rise from d to c is determined. Because of the large cross-section of B, the

pressure remains practically constant at 600 mm., varying not more than 1 mm. during the flow of the oil from one bulb to the other.

(*f*) The temperature is kept constant in *D* by means of the burner, the stirrer and by the addition of hot or cold water. A paraffin bath is used for temperatures above 90° C.

(*g*) **Calculation of the absolute viscosity.** By dividing the time of efflux of the oil by the calibration value for the capillary, a value for the specific viscosity of the oil is obtained, referred to water at 0° C. as unity. By multiplying this value by the absolute viscosity of water at 0° (0 01797), the absolute viscosity of the oil is obtained.

Example:

Tube III, time of efflux of the oil at 50° 728.3 seconds.

Tube III, calibration value (water equivalent) 53.3 seconds.

Dividing 728.3 by 53.3, the value 13.7 is obtained for the value of the specific viscosity (η) of the oil at 50°; multiplying this value by 0.01797, the absolute viscosity at 50°, $[\eta] = 0.246$, is found.

(*b*) Determination of Viscosity by the Falling Weight Method

This method is used with very viscous materials, such as glue or printer's ink, method (*a*) taking too much time. The principle of this method was developed by Stokes.

$$u = \frac{(2)\ (r^2)\ (g)\ (s - m)}{(9)\ (\eta)}$$

In this expression μ is the velocity of fall of a sphere, of radius r and density s, m is the density of the material under examination, the viscosity of which is η, and g is the acceleration of gravity.

In the determination of the viscosities of lithographic and similar varnishes, M. Stange has found the following method very useful. (Fig. 12.)

The cylindrical container (*A*) of 50 mm. inside diameter has a mark placed at the height of 150 mm. The sphere (*B*) of 40 mm. diameter is supported by a counterweight (*D*); this counterweight weighs 10 grams less than the sphere immersed in water. The fall of the sphere is limited by the distance that (*E*) can move; this distance is exactly 100 mm.

At the beginning of the experiment (*E*) and (*B*) are held high by the electromagnet (*H*); the current through I and II is broken by pushing (*M*), the weight beginning to fall. The current now passing through II and III, the electromagnet (*Q*) starts the clock (*O*). By releasing the pressure on (*M*), the current is switched to the electromagnet (*P*) and the contacts (*G* and *F*)· when (*E*) touches (*X*), the circuit is closed and the clock stopped by (*P*).

The vessel (*A*) hangs in a bath of mineral oil; this bath is kept at a constant temperature of 20° C. by means of the cooling coil (*S*), the electrical heating coil (*J*), and the sensitive electrical thermo-regulator (*K*). A stirrer (*R*) is also used.

(J) is attached to the lighting circuit and the relay (U V L); the electromagnet (U) is connected with a storage cell. The current is regulated by the mercury contained in the regulator (K).

The apparatus gives very satisfactory results, the variation on repetition and with different samples of the same material being not more than 1 per cent. The temperature is easily maintained. The certainty of the results has made unnecessary the keeping of comparison samples. The figures obtained for the time of fall with different samples varied from 4 seconds to 1.5 hours. With very viscous samples, the testing may be more easily done at 30 or 35°.

The time of fall is determined and compared with normal values obtained from satisfactory samples.

The most viscous printer's ink which could be examined by the capillary viscosimeter gave a value for the absolute viscosity [η] of 39.4; referred to water at 20° C., the specific viscosity (η) of this sample would be 3936, since the absolute viscosity of water at 20° is 0.01004.*

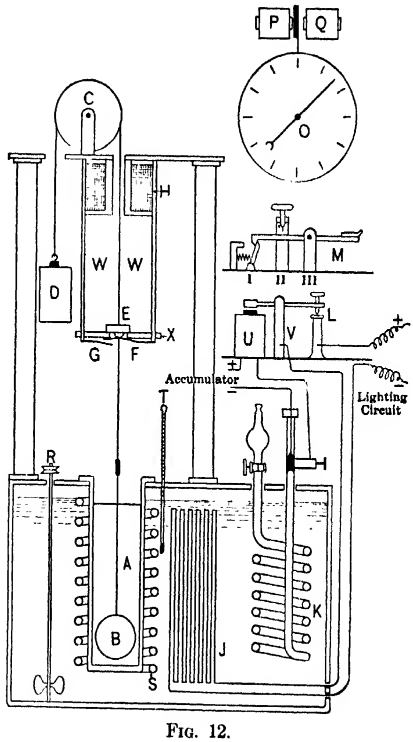


FIG. 12.

K. Arndt † has also constructed an instrument for the measurement of viscosity which depends upon the time required for a ball to fall; it

* From this it follows that the specific viscosity of liquids referred to water at 20° may be obtained by multiplication of the absolute viscosity of the material by the quotient $\frac{100}{1.004}$ (or by 100 for approximate values). See page 15.

† Handbuch der physikalisch-chemischen Technik, Enke, 1915, 506.

is mentioned here because of its simplicity and because of the ease with which it may be set up in ordinary laboratories. Arndt and Gessler in calibrating the instrument found the same values for the viscosity of castor oil that Kahlbaum and Raber had found by the capillary method.

(*c*) Values for Various Liquids

Table 2 and Figures 13 and 14 give the values of the absolute viscosities of several fatty oils, mineral oils, turpentine oil, tar oil, benzol, and water at different temperatures.

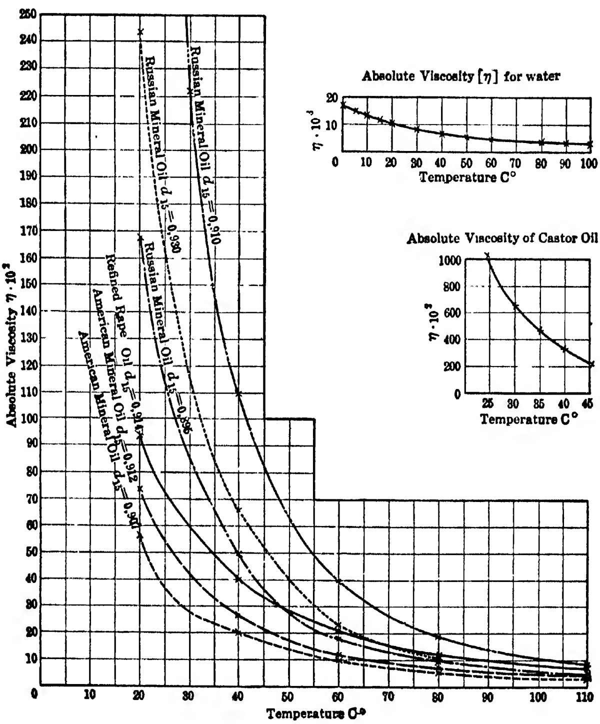


FIG. 13.

These figures emphasize the recognized and important fact that mineral oils lose their viscosity to a far greater degree with a rise of temperature than do fatty oils; it is also seen that compared with fatty oils, water loses its viscosity with increase of temperature to a less

marked extent. Figure 14 shows how very much tar oil, obtained from the high-boiling lubricating oil fraction of tar, loses in viscosity as the temperature rises.

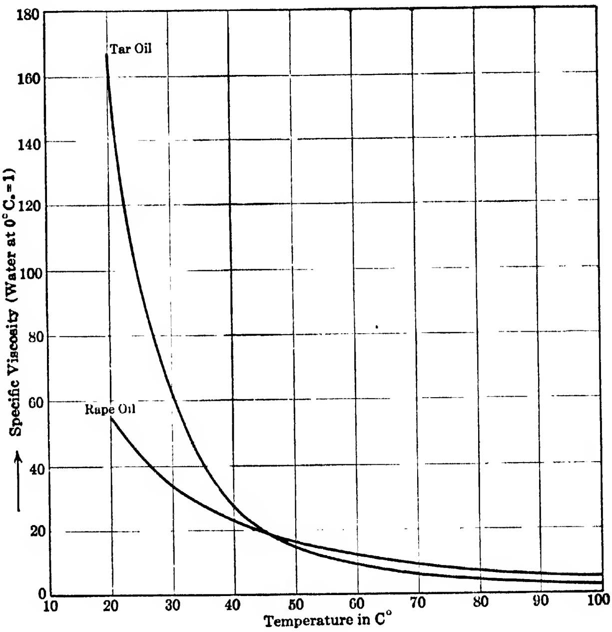


FIG. 14.

From the values given for 150° C., it is seen that for temperatures higher than this, as in the steam cylinder, viscosity determinations for mineral oils have little significance, because the observable differences have as yet received no industrial interpretation.

TABLE 2

ABSOLUTE VISCOSITY [η]

Material	Specific Gravity at 15° C.	at 20° C.	at 30° C.	at 40° C.	at 50° C.	at 60° C.	at 80° C.	at 110° C.	at 150° C.
Refined Rape Oil*.	0.914	0.928	0.589	0.405	0.281	0.207	0.119	0.070	0.043
Mustard Oil*	0.916	0.897	0.580	0.386	0.261	0.187	0.108	0.0705	0.043
Olive Oil*	0.915	0.920	0.593	0.405	0.240	0.197	0.130	0.0703	0.043
American Mineral	0.907	0.559	0.273	0.198	0.143	0.097	0.0583	0.0297	
Oil* .	0.912	0.735	0.417	0.262	0.176	0.1205	0.0718	0.0443	0.0137
	0.895	1.673	0.841	0.495	0.265	0.1717	0.0940	0.0434	0.0283
Russian Mineral	0.910	5.31	2.22	1.087	0.637	0.396	0.1825	0.0817	0.0426
Oil* . .	0.930	2.425	1.178	0.649	0.409	0.2315	0.1098		
German Mineral	0.915	1.520	0.870	0.446	0.282	0.186	0.0963	0.0578	0.0290
Oil*	0.923	4.245	2.107	1.100	0.585	0.403	0.2165	0.0831	0.0293
Water†	0.999126	0.01004	0.00802	0.00657	0.00553	0.00510	0.00360		
Castor Oil†	0.967	9.6	4.6	2.3					
Turpentine Oil†	0.870	0.1487	0.01272	0.01071	0.00926	0.00821	0.00671		
Hexane†	0.6654	0.00326	0.00296	0.00271	0.00248	0.00229			
Heptane†	0.6885	0.00416	0.00375	0.00341	0.00310	0.00284	0.00241		
Octane†	0.7188‡	0.00542	0.00483	0.00433	0.00391	0.00355	0.00297	0.00233	
Ethyl Ether†.	0.7201	0.00245	0.00223						
Ethyl Alcohol†	0.7936	0.01194	0.00992	0.00831	0.00701	0.00596			
Benzol† .	0.8846	0.00654	0.00567	0.00498	0.00444	0.00398	0.00336		

* Mitteilungen aus dem Kgl. Materialprufungsamt zu Berlin, **9**, Erganzungsheft V, Tab. 5, (1889). The values of the absolute viscosity have been recalculated by the Ubbelohde formula from the Engler degrees determined by Holde.

† Landolt-Börnstein-Roth, Tabellen, pages 75 to 80.

‡ At 0° C. || At 15° C., the value is 0.989.

(*d*) The Unit for Viscosity

This question does not seem settled. Ubbelohde* has pointed out some of the difficulties. Physicists and physical chemists use besides the absolute viscosity, expressed in c.g.s. units, the specific viscosity referred to water at 0° C. (or the temperature of experiment, say 20°).

The use of the absolute viscosity would seem to be always permissible; but since these values are generally small, for water at 0° the value is 0.01797 and at 20° it is 0.01004, it may be more advantageous to use numbers 100 times as large. The general tendency in the scientific literature and in industrial practice to make comparisons would seem to justify the use of a so-called specific viscosity, a value referred to some convenient temperature.

* Petroleum, **7**, 773,882,938 (1911); see also Technologic papers of the Bureau of Standards, Numbers 100, 112, 125 and 164 by W. H. Herschel, Washington, D. C., (1917 to 1920).

For this purpose probably water at 20° C. is the best material to serve for reference. Since at 20° the absolute viscosity of water is 0.01004, to obtain the specific viscosity of a material referred to water at 20°, it is only necessary to multiply by the quotient $\frac{100}{1.004}$. Since for all practical purposes this quotient may be taken equal to 100, we have here a very convenient standard of comparison. The specific viscosity (η) of an oil referred to water at 20° C. is therefore 100 times the absolute viscosity $[\eta]$.

This may be seen in the following tabulation:

Oil Number	Engler Degrees	Absolute Viscosity	Specific Viscosity referred to water at 20° = 1.	
			$\times$ 100	$\times \frac{100}{1.004}$
1	1.26	0,0359	3.59	3.58
2	16 4	1.131	113 1	112.7
3.	19.7	1.347	134.7	134.1
4.	41.1	2 86	286.	285
5.	53.6	3 76	376	375

This table shows the advantages of this method of stating viscosities, and also shows the inadequacy of the "Engler degrees" which not only have no connection with the c.g.s. system but in the more fluid oils do not even have any direct relation to the true viscosities in question. The same statement may be made with regard to the Saybolt, the Redwood and the Nobel degrees.

In order to get away from such arbitrary scales, it is desirable to supplant such values by others expressed in c.g.s. units (such as the Poise = one dyne-second per square centimeter). Ubbelohde* has suggested a formula for transforming "Engler degrees" to specific viscosity (referred to water at 0° C.), as follows:*

$$(\eta) = \left(4.072\,\mathrm{E} - \frac{3.518}{\mathrm{E}}\right)(\text{sp. grav.})$$

* Holde finds that this formula, when checked by the capillary method does not always give correct results; with oils with "Engler degrees" ranging from 7 to 615, the calculated specific viscosity must be increased by 4.2 per cent. With this correction, the specific viscosity may be calculated to within 1 per cent. But if the "Engler degree" is less than 7 an additional correction is necessary. An oil with Engler value 5 gave a calculated specific viscosity which was 8 per cent in error.

Meissner* has prepared such comparison values from empirical efflux experiments, and has found relations different at 50° than at 20°, with the Engler, Redwood and Saybolt viscosimeters.

The American reader is referred again to the valuable work in this connection by Herschel, published as Technologic Papers of the Bureau of Standards, Numbers 100 and 112, at Washington.

(c) Industrial Viscosimeters

Glass viscosimeters are easily broken, are rather hard to calibrate, are not easily replaced, and their manipulation requires considerable skill. For the last forty years therefore metal viscosimeters have been used in industrial work. The time of efflux of the oil divided by the time of efflux of water (or rape oil) at 20° gives a value which is compared with others of the same nature.

These viscosimeters do not allow the direct determination of the absolute internal friction or the specific viscosity; they give a not always exact but at least a relative comparison of the viscosity of oils. The expression of Poiseuille† applies only so long as the outflow tube is really a capillary, and only so long as there is a certain ratio between the length and diameter of the capillary, this ratio depending upon the radius, the liquid and the temperature. Herschel points out that the value of the product of the velocity of flow and diameter of the tube, divided by the so-called kinematic viscosity, must not be greater than 800 if the flow is to be viscous rather than turbulent.

All the viscosimeters used industrially (including the Engler) have improperly proportioned outflow tubes and therefore do not give absolute values but only relative ones; these values have however been everywhere used, especially in the examination of mineral oils, and seem to be indispensable.

In Germany the Engler has been officially adopted, in England the Redwood instrument is used, the Nobel-Lamansky apparatus is used in Russia, while the Saybolt viscosimeter is widely in use in the United States.

1. Engler Viscosimeter

There are several types of the Engler apparatus. These all have the same dimensioned container and outlet tube; they vary only in regard to the method of heating, etc. Figure 15 shows the type used by Holde. The oil-container is

* Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse und Harze, **19,** 30, 44 (1912); **20,** 123 (1913); **21,** 28 (1914).

† Petroff, Neue Theorie der Reibung, Voss, 1887; Hagenbach, Poggendorf Annalen, **1860,** 365; Rakusin, Untersuchung des Erdols, 131.

filled to the marks with oil, the platinum outlet tube being closed by the wooden plug. The temperature of the oil is regulated by heating water in the outer vessel; the ring burner is adjustable. The outflowing oil or water is caught in the graduated flask which has a 200 c.c. mark, as well as a mark for 100 c.c., as a check for each experiment.

The time of outflow of 200 c.c. oil at the temperature of the experiment divided by the time of outflow of water at 20° C. gives the so-called "Engler degree."

The heating bath is kept closed, so that with water, temperatures up to and including 100° may be used; for higher temperatures other liquids may be used (see page 543) but oil must not be used as the liquid for temperatures above 90° as overheating of the outlet tube may easily occur. To become independent of fluctuations of the atmospheric pressure, and to allow the use of water for the maintenance of a temperature of 100° in the container, a slight excess of pressure may be produced in the heating bath by attaching an inverted U-tube, one end of which dips below the surface of mercury kept in a test tube.

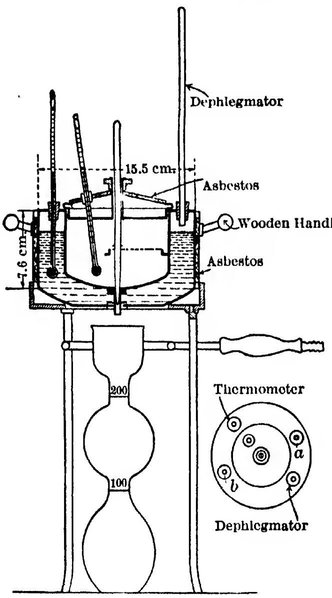


FIG. 15.

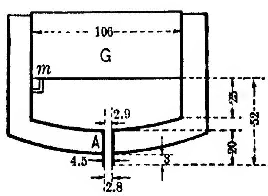


FIG. 16.

The following are the official dimensions of the Engler apparatus as adopted by the different testing laboratories of Germany.*

1. **Dimensions** (Fig. 16).

(*a*) For the gilded vessel *G*.

Width (inside diameter)	106 mm. ± 1 0 mm.
Height of the cylindrical part below the marks *m*	25 mm. ± 1 0 mm.
Height of the marks *m* above the lower end of the jet	52 mm. ± 0.5 mm.

(*b*) For the platinum jet *A*.

Length of jet	20 mm. ± 0 1 mm.
Inside diameter of jet, upper end	2 9 mm. ± 0.02 mm.
Inside diameter of jet, lower end	2.8 mm. ± 0.02 mm.

* Chemiker-Zeitung, **31**, 441 (1907).

Length of jet projecting from the lower part of the outer vessel	3.0 mm. ± 0.3 mm.
Width	4.5 mm. ± 0.2 mm.

The jet may be made of platinum or lined with a sufficiently thick layer of platinum but the interior must be smooth and not wavy.

(*a*) **Determination of the Time of Outflow of 200 c.c. of Water at 20° C.** This value should be frequently checked, at least once every six months. The vessel is first washed with ethyl ether or petroleum ether, then repeatedly with alcohol and finally with distilled water (Fig. 15). The apparatus is then set horizontal. The wooden plug, which is used only for water and should not have touched oil, is inserted. The measuring flask, filled nearly to the top with water at 20°, is emptied into the inner vessel, thus covering the gage points *m*. By means of the outer bath the water is kept at 20°. By cautious manipulation of the plug the jet is entirely filled with water and the bottom is wet so that a drop remains hanging and covers the entire surface. To bring the height of the water to that of the levelling studs, the excess is removed with a pipette. After the apparatus has been thus prepared the time (to $\frac{1}{5}$ of a second) necessary to fill the measuring flask up to the 200 c.c. mark is determined (the water surface being perfectly quiet). The experiment is repeated several times; when three tests give results varying not more than 0.5 second, and the values have not decreased systematically, the first series may be considered completed. The apparatus is again cleaned and the tests repeated; if these results agree with the first series, further tests are unnecessary, otherwise they must be continued to constancy. From the six values of the last two series, the mean value for the time of outflow is obtained; and rounded off to 0.2 second, this is the calibration value of the instrument. With a properly built apparatus the time of outflow should be between 50 and 52 seconds.

Exact determinations should be made in a room of approximately 20°. The thermometers should be standardized.* The measuring flasks should be dry and should have been standardized for content.

(*b*) The cleaned apparatus is filled to the gage points with oil which has previously been passed through a sieve (0.3 mm. mesh).

At higher temperatures, before filling with oil, the bath should be pre-heated so that the oil may rapidly attain the required temperature; the temperature is adjusted by stirring the oil, by raising the cover, by agitating the water in the bath with the air-stirrer, or by adding cold water to the bath.

When the proper constant temperature is obtained, the measuring flask is placed in position and the plug is lifted. The exact time in seconds necessary for the oil to fill the flask to the 100 c.c. and 200 c.c. marks is noted.

The mean of two determinations at each temperature is taken. Generally five determinations are made between 20° and 50°, or six between 20° and 150°; the results are plotted on co-ordinate paper, a curve being drawn. Intermediate values are read from the curve.

The results check well. Below 50°, the values for ordinary oils agree to within 0.5 per cent; with heavy machine oils, the variation may be 1.5 per cent, with cylinder oils, as much as 3.5 per cent. Two

* Zentralbl. f. d. deutsche Reich., **1898,** No. 6.
Mitteilungen d. Kais. Normaleich.-Komm. 2 Reihe. Nr. 17 (1904).

instruments, with the same oil, may give results which differ as much as 2.5 per cent. Oils used at ordinary temperatures (spindle and machinery oils) should be tested at 20° and at 50° C.; cylinder oils at 50° and 100°. In the case of superheated-steam cylinder oils, which are often subjected to temperatures above 300° C., determinations at 180° or at 200° may be expected. Generally however determinations at + 50° and at + 100° are enough, as at the high temperatures the differences in the viscosities of different oils become very small. For high temperature work, special heating baths are used, using high boiling liquids to heat the Engler container. It has also been suggested that for such high temperature work, a viscosimeter, constructed with a very narrow orifice and an exceptionally long outflow tube, would show greater differences in time of outflow than does the Engler apparatus; the results would not however be directly comparable with the "Engler degrees."

(*c*) Certain dark oils, containing suspended solid paraffin or pitch particles, may give widely different values when tested by the Engler viscosimeter. By heating before testing, the viscosity decreases; by cooling before testing, the viscosity at 20° is greater. The variation may be 15 per cent. Pale and dark distillates, which show no paraffin or pitch particles in thin films, do not show such differences. It is evident that this behavior is due to partial melting on warming, and partial separation of solid paraffin or pitch particles on cooling; this has been confirmed by noting the behavior of artificial mixtures of paraffin and pale oils.

If on examination of a thin film of oil, solid paraffin or pitch particles are recognized, it is well to expect from 7 to 8 per cent variation in the viscosimeter readings. To get results which check, it may be well, after making the usual experiments, to also make readings with some of the oil which has been heated for 10 minutes at 100°, and with a sample which has been cooled to − 15°. In case of dispute about specifications, the latter method must be followed. Generally however oils containing solid particles are tested at 50°, at which temperature variations in the degree of fluidity do not usually appear.

(*d*) **Shorter Methods.** Martens has suggested the use of a quadruple apparatus (Fig. 17) in which four Engler containers are heated by one large water bath (*W*). The temperature is regulated by means of the stirrer (*T*), run by the turbine (*RS*), by the addition of cold water, or by a small gas flame.

For experiments at 100°, boiling water and the mercury pressure arrangement of Holde, previously mentioned, may be used.

The determination of the time of outflow of smaller amounts of liquid but with normal filling allows the shortening of the procedure. One of the disadvantages of the Engler apparatus is the long time required for the discharge of 200 c.c. of oil. This is avoided* by noting the time necessary to discharge a small volume of oil and calculating the time of discharge of 200 c.c. It has been found that there is a definite relation between the discharge of the small volume and that of the 200 c.c. The time of efflux of 20 c.c. is multiplied by the factor 11.95; the factor for 50 c.c. is 5.03; for 100 c.c., it is 2.353. In each case the time of discharge of 200 c.c. of oil is obtained; these relationships hold true for all oils which require at least 3 minutes for the time of discharge, that is, have an Engler degree of more than 5. Thin oils should not be so tested.

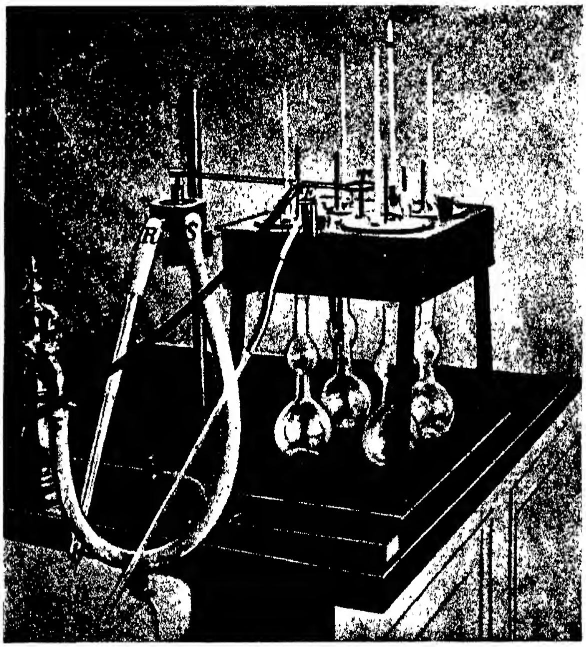


FIG. 17.

The Ubbelohde tables† allow the direct reading of the Engler degree

* Petroleum, **2**, 555 (1906).

† Published by S. Hirzel, Leipzig.

of 200 c.c. of oil from the observed time of outflow of 50, or 100, or 200 c.c. for instruments having a calibration value for water of from 50 to 52 seconds.

(*e*) If the amount of oil available for experiment is small, it may be necessary to determine the time of outflow with less than 200 c.c. of oil in the container. This may be necessary if mineral oil to be examined has been extracted from a mixture of fatty and mineral oil; in this case probably only a small sample would be available.

In such a case 45 c.c. of oil should be put into the container at 20° C. and time necessary for 20 c.c. to discharge should be noted. By multiplying this observed time by 7.25, the time of discharge of 200 c.c. with normal filling would be obtained.

Other quantities of oil might be used, and the time of discharge of still smaller volumes noted; by use of proper factors, the Engler degree can be calculated.* The following factors have been determined:

Initial filling (c.c.)	25	45	45	50	50	60	120
Amount run out (c.c.)	10	20	25	20	40	50	100
Factor	13	7.25	5 55	7 3	3.62	2.79	1.65

(*f*) Ubbelohde† has had built by Sommer and Runge an ordinary Engler apparatus, threaded at the bottom to receive a smaller, narrower containing vessel which has $\frac{1}{10}$ the capacity of the larger container. This smaller vessel allows the use of only 20 c.c. of oil. (Figure 18.)

The smaller vessel has only one gage point. The plug carries a ball on the end, which fits into a hemi-spherical depression above the outflow tube. The inner tube can be removed and the outer vessel used as usual to determine the Engler degree with 200 c.c. portions. When using the smaller

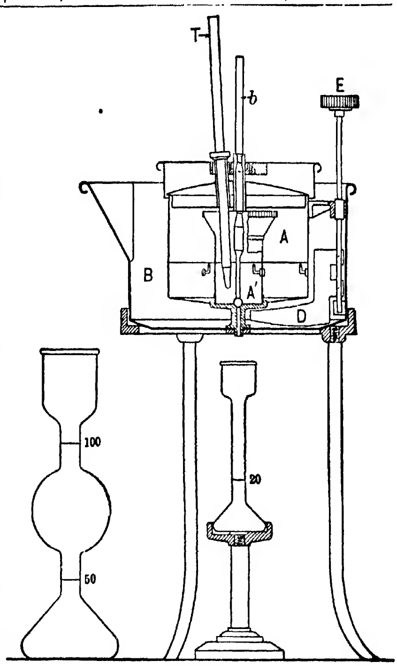


Fig. 18.

* Mitteilung., **17**, 63 (1899); Gans, Chem. Rev., **6**, 218 (1899); Offermann, Chem. Rev., **18**, 272 (1911).

† Scheel, Petroleum, **12**, 873 (1917).

vessel, the larger container, as well as the usual heating bath must be filled with a heating liquid.

The dimensions of the larger vessel and the outflow tube are those of the official Engler apparatus. Because of the greater relative volume of the thermometer and the plug, the dimensions of the smaller, inner vessel must be properly adjusted; the internal diameter of the inner vessel should be 33.8 mm., the gage point should be 52.5 mm. above the lower end of the jet.

According to the investigations of the German Physikalisch-Technischen Reichsanstalt, such an apparatus, of proper dimensions, the inner vessel of one-tenth the usual capacity, will give the same value for the Engler degree as the regular container, provided the time of outflow of water is considered in each case. As it is difficult to determine the exact time of outflow in the case of water with the smaller vessel, the German Reichsanstalt will determine and certify the values for each instrument.

(*g*) If less than 20 c.c. of oil are available, the capillary viscosimeter (Fig. 10, page 9) should be used; Ubbelohde has suggested a formula for calculating the Engler degree from the time of flow through the capillary.

Example:

Engler value greater than 10.
Temperature of experiment was 20° C.
Calibration value of the capillary (water at 0° C.) was 1.271.
Specific gravity of the oil at 20° was 0.9132.
Time of efflux of the oil at 20° was 135 seconds.
Ubbelohde calculates the Engler degree with the following expression:

$$E = \frac{\text{Time of efflux in seconds}}{(\text{Calibration value at } 0^\circ)\ (\text{sp. grav. of oil})\ (4.072)}$$

$$= \frac{135}{(1.271)\ (0.9132)\ (4.072)} = 28.6$$

The Engler degree of the oil is 28.6. In the above expression, the time of efflux of the oil at the temperature of the experiment has been substituted; similarly the specific gravity at that temperature has been used.

We have already mentioned the Ubbelohde formula for conversion of Engler degrees into specific viscosity; in this, the specific viscosity is referred to water at 0° C. as unity, the Engler degree however is referred to water at 20° C. as unity.

$$(\eta) = \left(4.072\,E - \frac{3.518}{E}\right)(s)$$

In this (η) is the desired specific viscosity, (s) is the specific gravity and (E) the Engler degree, both at the temperature of the experiment.

Substitution of different values in this expression will show clearly that in some cases the specific viscosity is about 0.6 the value of the Engler degree, while in other cases it may be 4.4 times as great as the Engler degree. The reason for this is probably to be found in the fact that the outlet tube of the Engler apparatus is so large that the Poiseuille formula does not apply. In the discharge of liquid from the Engler apparatus, two factors must be considered; one is the work necessary to give the liquid its motion, and the other is the work necessary to overcome its viscous resistance. Engler degrees should therefore not be used in hydrodynamic calculations.

If we were to substitute the constants for water in the above expression, we would find at 20° that the first term would have the value (4.072) (1), the negative term would have the value $\frac{3.518}{1}$ while the specific gravity would be 0.999. This would give a value for the specific viscosity of 0.558 (actual is 0.01004). The negative term is about six times as large as the specific viscosity calculated; this term represents the work necessary to set the water in motion. This work in the Engler apparatus, because of the high velocity of efflux, is about six times as great as the work necessary to overcome viscous resistance.

With higher viscosity (when Engler degrees become larger) the first term of the expression becomes larger, and the second term becomes smaller. When the Engler degree is 5, the negative term still represents 5 per cent; with Engler degree 10, the negative term is only 1 per cent. For values of E greater than 10, it is allowable to use the simplified expression:

$$(\eta) = (s)\ (4.072)\ (E)$$

Attention is again called to the experience of Holde that values obtained by the Ubbelohde expression must be increased by 4 per cent.

2. The Lamansky-Nobel Viscosimeter

This,* as well as the Engler apparatus, is used in Russia. Figs. 19 and 20.

The metal outflow vessel A has at the bottom a metallic block D serving as the jet, the opening of which can be closed by a metal rod M which has a pointed wooden end serving as a plug. The water bath B is used for heating, this being warmed with steam from C. A stirrer H is attached.

After filling the vessel A with oil (about 400 c.c. are necessary) and getting a constant temperature, the oil will run out on raising M (at constant pressure of 200 mm., obtained by a Mariotte tube F dipping into the oil). The opening at E

* Wischin and Singer, Chem. Rev., 4, 89, 243 (1897).

should be so wide that the time of outflow of 100 c.c. of distilled water at 50° and 200 mm. pressure height will be 60 seconds (± 1). The length of the jet should be exactly 10 mm. The tests are made at 50°.

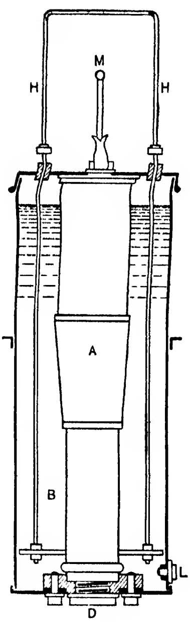


FIG. 19.

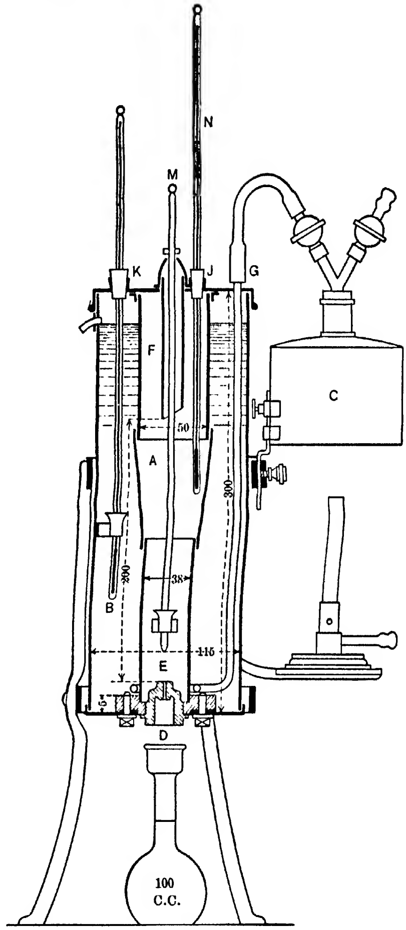


FIG. 20

The viscosity is the quotient obtained by dividing the time of outflow of 100 c.c. of oil by the time of outflow of 100 c.c. of water at 50° C.

The faults of the method are the difficulty of cleaning, the attention required and the large amounts of oil necessary (see remarks on the shortening of the Engler procedure). On the other hand because of the constant pressure, the time of outflow of 100 c.c. can be calculated directly from the time of outflow of a small amount.

The relation between the viscosities obtained by the **Lamansky-Nobel** and the Engler apparatus is fairly constant.

$$\frac{\text{Lamansky-Nobel Viscosity}}{\text{Engler Viscosity}} = 1.13 \text{ to } 1.18.$$

For viscous machine oils and for cylinder oils the ratio is 1.20 to 1.26.

3. **The Redwood Viscosimeter.** (Figs. 21 and 23.) This instrument holds approximately the same place in England that the Engler holds in Germany, only the definiteness of the dimensions of the apparatus is not so great as in the case of the Engler.

It consists of a silvered copper oil-container C about $1\frac{7}{8}$ inches in diameter and $3\frac{1}{2}$ inches high. The bottom has an agate jet, a depression of which is closed with

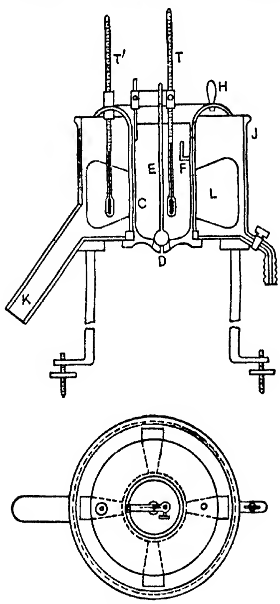


FIG. 21.

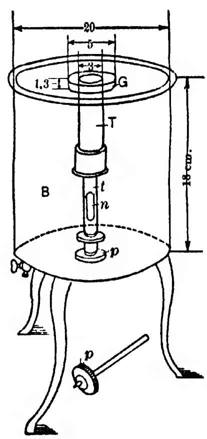


FIG. 22.

the rod E. The temperature of the liquid is kept constant by the stirrer (wings L and grip H).

Method. For temperatures up to 95° the bath J is filled with water; for higher temperatures, with suitable mineral oil. The oil to be tested is filtered and dried and brought to the temperature of the bath, then filled to the mark F. A narrow-necked 50 c.c. flask is put under the jet in a vessel with liquid at the temperature of the oil. The plug is raised and the time of filling the flask to the 50 c.c. mark is observed.

4. **The Saybolt Viscosimeter** (Figs. 22 and 24). This is much used in the United States.

It consists of a cylindrical brass tube (T), 8 cm. long and 3 cm. in diameter, (of about 66 c.c. volume) with an over-flow arrangement at the top; it terminates at the bottom in a metal jet about 1.75 mm. in diameter. The entire apparatus is embedded in a water bath B. The bottom is closed with a stopper which does not touch the jet. When the oil is filled into T the excess overflows to the gallery from which it can be removed by a pipette. The apparatus is heated to 70° F. or 21.1° C., the stopper removed from the bottom and the time for 60 c.c. to flow out determined. At higher temperatures a narrower mouthpiece of $\frac{3}{64}$ inch or 1.19 mm. is attached. Recent investigations have shown that the different Saybolt viscosimeters in use sometimes show differences with regard to each other; consequently the values found with one instrument are not directly transferable to another.

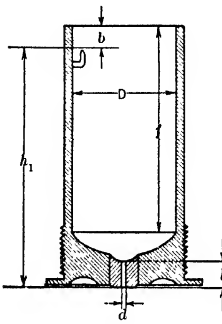


FIG. 23.

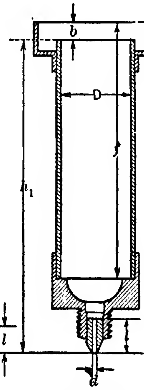


FIG. 24.

TABLE 3

	Redwood, cm.	Saybolt universal, cm.
Diameter of the outflow vessel D	4.655–4.691	2.968
Original height of liquid h'	9.328–9.615	12.688
Length of the jet l	0.986–1.023	1.411
Mean diameter of the jet d_m	0.158–0.163	0.178
Dimensions of parts of the diagram b	0.900	0.708
Dimensions of parts of the diagram f	8.64	10.35

The essential points of the Redwood and the Saybolt instruments are shown in cross-section in Figs. 23 and 24. The figures given were found by Meissner.* (Table 3.) The efflux volume of the Redwood instrument is 50 c.c., of the Saybolt apparatus, 60 c.c.

The summary below gives the normal dimensions and allowable variations of the Saybolt viscosimeter proposed by the United States Bureau of Standards and accepted by Mr. Saybolt October 1, 1917.

* Chem. Rev., **19**, 30 (1912); **20**, 123 (1913).

The tolerances were determined by a compromise between two considerations. Too much tolerance would cause too great a variation in efflux time between different instruments, while too small a tolerance would unnecessarily increase the cost of manufacture in attempting to obtain a degree of accuracy not required in technical work. For precise scientific work, some form of viscosimeter should be used which is provided with an outlet tube of much greater length as compared with its diameter.*

DIMENSIONS OF THE STANDARD SAYBOLT UNIVERSAL VISCOSIMETER

Dimensions	Minimum	Normal	Maximum
	Centimeters		
Diameter of outlet tube	0.175	0.1765	0.1780
Length of outlet tube	1.215	1.225	1.235
Outer diameter of outlet tube at lower end	0.28	0.30	0.32
Height of overflow of rim to the bottom of outlet tube	12.55	12.60	12.65
Diameter of container	2.995	2.975	2.995
Average head (calculated)	7.32	7.47	7.61

The time of outflow T_R of the Redwood instrument and T_S of the Saybolt instrument can be referred to the normal Engler apparatus as follows:

$$T_R = 192.2\,k\left(1 + \sqrt{1 + \frac{0.01624}{k^2}}\right)$$

$$T_S = 228.7\,k\left(1 + \sqrt{1 + \frac{0.01309}{k^2}}\right),$$

$$k = 0.08019\,E - 0.07013\frac{1}{E}.$$

The values calculated in this way for the Redwood instrument are accurate to 4 per cent; with the Saybolt apparatus they are accurate to within 2 per cent.

By direct comparison at different temperatures, it has been found that at 20° C. the ratio of Redwood degrees to Engler degrees ranges from 1.038 to 1.109; at 50° C. the ratio varies from 1.148 to 1.180. Up to $E = 15$, the ratio of Redwood to Engler degrees increases, above that value it decreases.

* Technologic Papers of the Bureau of Standards, **110**, page 12; **112**, page 7.

5. The Metal Viscosimeter of Holde

In spite of many improvements, the Engler viscosimeter still has disadvantages. These have in part been due to its dimensions which have been accepted as a matter of custom. One of the disadvantages is the poor heating arrangement, due to the wide oil container which makes the attainment of a constant temperature difficult; another is the wearisome adjustment of the oil level by means of the gage points, which must be repeated with every repetition of the experiment, with every change of temperature the container must be opened and the level adjusted.

Holde has attempted to use his experience of many years in the determination of viscosity for industrial purposes in designing an apparatus which avoids the deficiencies of the Engler apparatus. The viscosimeter* was constructed during the war, and has given satisfaction, but requires further trial.

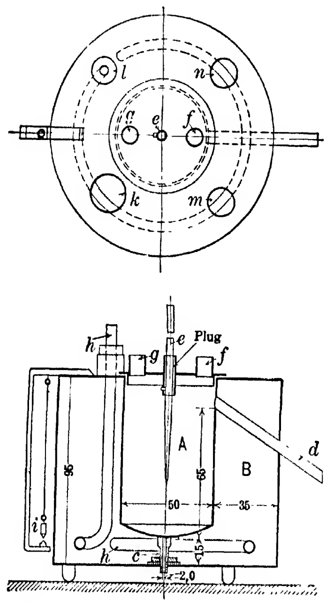


FIG. 25.

See Figure 25 for plan and elevation; Figure 26 gives a general view. See also Figure 93, page 177.

The oil container has a diameter of 50 mm. instead of 106 as in the Engler apparatus; the height of liquid is greater (80 mm.). The gage points are missing, an overflow tube being provided. A stirrer (*h*) allows agitation of the heating liquid by means of the hand bellows; this may not be absolutely necessary as the water can be kept at constant temperature (within 0.2°) when water is the heating liquid. For experiments at 100°, the pressure regulator (page 177) already mentioned allows easy maintenance of constant temperature; the mercury allows a slight excess pressure to exist, compensating for the difference of air-pressure from normal. To keep the container at 100°. it is necessary to heat the bath to a slightly higher temperature, because of radiation and convection.

The time of efflux of 25 and 50 c.c. or of 50 and 100 c.c., or only of 100 c.c. was determined, depending upon the classification of the oil as very viscous, viscous, or mobile. To calculate the time of efflux of 100 c.c. from the observed time of 50 c.c., the factor 2.65 was used; the factor for 25 c.c. was found to be 5.91.

* Built by R. Heiser, Lichterfelde; obtainable from Sommer & Runge Berlin.

TABLE 4

	II					III				IV				V				VI	VII				VIII			
	Specific Gravity × 10000					Engler Degree				Specific Viscosity (η) (Water at 0° = 1) calculated from III				Specific Viscosity (η) + 4 % (Water at 0° = 1) calculated according to Holde				Actual determination of (η) Capillary Method	[η] Absolute Viscosity from V (V) (0 01797)				Efflux time in seconds of 100 c.c. in new Holde apparatus H			
	15°	20°	25°	50°	100°	20°	25°	50°	100°	20°	25°	50°	100°	20°	25°	50°	100°	20°	20°	25°	50°	100°	20°	25°	50°	100°
1	8227	8193				1 26				1 92				2 0				1 78	0 036				62			
2	9094	9060		8856		16 4		3 7		60 4		12 6		63 0		13 1		64 9	1 13		0 24		1019		223	
3	9023	8989		8785		19 7		4.0		71 9		13 4		75 0		13 9		74 9	1 35		0 25		1247		257	
4	9084	9050	9016	8846		41 4	28 8	6 4		152 5	105 6	22 7		159	110	23 7		156 7	2 86	1 98	0 43		2642	1819	414	
5	9256	9222		9018	8678	53 6		7 2	1 7	200 7		26 1	4 3	209		27 2	4 4	212 4	3 76		0 49	0 08	3397		470	93
6	9193				8615				4 5				15 0				15 6					0 28				278

In Table 4 are given comparisons of six different, viscous oils, using the new viscosimeter, the Engler apparatus and the capillary viscosimeter. By plotting the time of efflux with the Holde apparatus as ordinates, and the absolute viscosity as abscissas, it is possible to draw a straight line through the points, deviation being evident only near the origin.

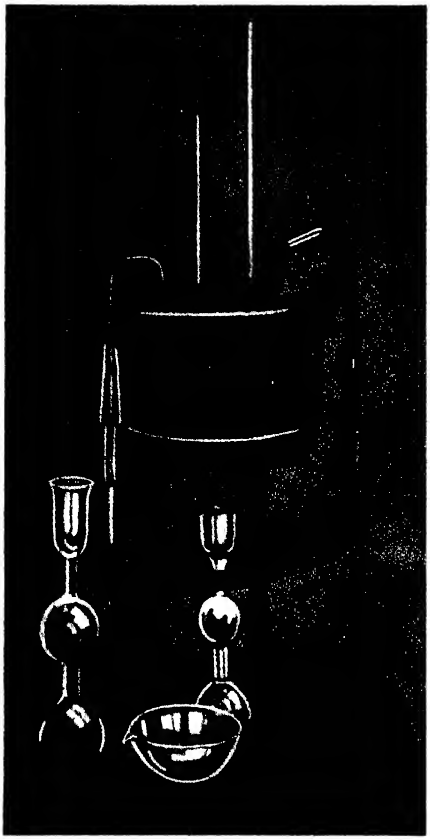


FIG. 26.

Transformation formulas and tables* have been prepared for calculating the Engler degree and the absolute viscosity into Holde (H) degrees. Thus

$$E = 0.114 + 0.015714\,H$$
$$[\eta](10^2) = -2.73 + 0.110704\,H$$

Using these expressions it is possible to calculate values from the results of the Holde apparatus which differ (with oils of absolute viscosity of more than 0.24) from the observed Engler or capillary determinations by not more than + 2.7 per cent; with more mobile oils ($[\eta]$ = 0.04 to 0.22) the error ranges from + 5 to − 12 per cent.

6. Calculation of the Viscosity of Mixtures

The viscosity of mixtures of oils cannot be calculated by the method of mixtures from the viscosities of the component oils; viscosity is not an additive property. The values of the actual viscosities are

* Scheel, Petroleum, 13, 705 (1917).

always less than the calculated. From experiments of Sherman, Gray and Hammerschlag* it appears that the relation between viscosity and the percentage composition of the mixture (viscosity as ordinates, percentage composition as abscissas) may be shown graphically by means of hyperbolic curves; the deviation from a straight line (which would be obtained by the law of mixtures) is larger the greater the difference in viscosity of the two component oils. With mixtures of fatty oils and mineral oils, the deviation from the calculated values is decidedly less than with mixtures of pure mineral oils.

It is often necessary to obtain an oil of definite viscosity by mixing two oils of known viscosity. To avoid the method of trial, F. Schulz† after experimenting suggested formulas by means of which he claimed it was possible to calculate what per cent of each oil would be necessary to give a mixture of desired viscosity.

It has however been shown by actual trial that the formulas of Schulz for mixtures from 5 to 95 per cent are absolutely unreliable. For example if the viscosity of a mixture of 50 parts of each of two oils, one of 12.7, the other of 9.5 Engler degrees, is calculated, the result obtained is 13.1; this is actually greater than the viscosity of the more viscous component. For a mixture of an oil of Engler value 19.7 with an equal volume of an oil of Engler value 16.4, one might expect by the Schulz formula the Engler value 22.3; actual experiment gave an Engler degree of 18.8 (the value which might have been calculated by the simple law of mixtures is 18.05).

IV. Surface Tension

The surface tension is important‡ in studying the action of lubricating materials on the surface of the bearing; it is concerned with the rise of lubricating and illuminating oils in wicks; and it plays a part in the calming of waves by oil, and in the formation of a lather by means of soap.

Up to the present it has not been customary in the analysis of fats and oils and of related products to determine their surface tensions for distinguishing between them; the differences have been too small. But in view of the above-mentioned application of these phenomena in the industrial use of fats and oils, it may be well to briefly discuss surface tension and describe means of measuring its effects.

Every liquid endeavors to assume the shape having the least super-

* Jour. Ind. and Eng. Chem., **1909**, 12; Zeit f. angew. Chem., **22**, 653 (1909).

† Chem. Rev., **16**, 297 (1909).

‡ Ubbelohde, Petroleum, **7**, 773 (1911).

ficial area. The force,* which, acting in the surface film, tends to prevent an increase of the surface, is known as the surface tension; it is numerically equal to the force acting at right angles to a line of unit length. This force is called the constant of capillarity (T).

While a soap bubble is being blown, before it has separated from the pipe, the surface tension tends to drive the air backwards through the pipe.† This may easily be shown by allowing this escaping air to strike the flame of a candle; the flame will either be deflected, or extinguished. After a finished bubble has been separated from the pipe, the inclosed air will be under a pressure (due to the surface tension); consequently on collapsing very small particles of liquid will be blown in all directions.

A freely floating liquid, on which no external force is acting, will always assume a spherical form (this has the smallest surface); this is the case with an oil suspended in a mixture of alcohol and water (of the same density as the oil, and in which the oil is not soluble). Several of such drops may coalesce, in which case a larger spherical drop will form.

In considering the measurement of surface tension, effects at the surface of contact between liquid and gas‡ need hardly be here considered; the cases, most important in the study of oils, are concerned with a solid surface. The most important of these are the methods of counting the number of falling drops, or determining the weight of the drops; the rise in the capillary is also very frequently used.

The size of drops has been often used for the determination of surface tension; it has not always been correctly applied. Presumably the drop is held to a circular surface by surface tension; when the drop is detached the surface tension effect is just overcome. The two quantities appear to be equal (weight = surface tension); unfortunately the weight of the falling drop is not the same as that of the hanging drop, in some cases being only $\frac{4}{5}$ the latter. Only under very special conditions does the weight of the falling drop appear to be clearly proportional to the surface tension.§

In the method in which the number of drops are counted, it is as-

* Arndt, Handbuch der physikalisch-chemischen Methodik, Enke, 512.

† Zehnder, Grundriss der Physik, II Auflage, Tubingen, 58 (1914).

‡ See Freundlich, Kapillarchemie, **1909**, 4, 14; Wiedemanns Annalen, **38**, 118 (1889); Drud. Annalen, **3**, 659 (1900); **4**, 367 (1901); **6**, 559 (1901); **9**, 1261 (1902).

§ Kohlrausch, Lehrbuch der praktischen Physik, 1914; Neuberg, Der Harn, Theil II, 1701; Ostwald-Luther, Physiko-chemischen Methoden, 3rd edition, 237 (1910); Poynting and Thomson, Properties of Matter, 161. Arndt, Handbuch der physikalisch-chenischen Technik, Enke, 512.

sumed that if two liquids with different surface tension are allowed to drop from the same tube, the size of the drops will be smaller with the liquid of less surface tension; the volume of a drop is assumed to be proportional to the surface tension, and the number of drops which fall in unit time (or which give a definite volume of liquid) is assumed inversely proportional to the surface tension.

Traube* has developed a method depending on this assumption. The bulb a of the stalagmometer (Fig. 27) S has a volume of from 6 to 8 c.c. To the bulb is attached a capillary tube of such diameter that 4 to 5 seconds are required for a drop to form at its lower end; the tubes above and below the bulb are graduated to 0.05 part of a drop, the volume of a drop being determined by trial. The dropping surface should be free from fat. To read the upper level, the top is closed for a moment with the finger when experiment begins. Sets of tubes for different liquids may be obtained. A thermostat as shown is advisable; 5° difference in temperature makes a difference of 1 drop in 100.

The liquid is sucked into the tubes to the mark; the number of drops in the contained liquid is then determined. In general, the liquid may be allowed to flow out because of its own weight; in more accurate work, a constant pressure should be applied. If Z is the number of drops at 15° for the liquid, and Z_w is the number of drops of water, the ratio gives values which are comparable.

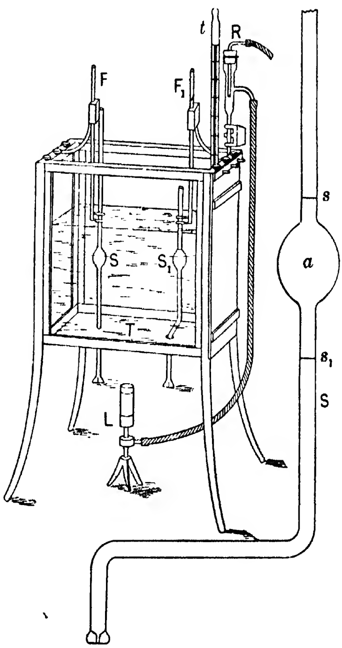


Fig. 27.

Probably the most satisfactory of all the methods is the one depending upon the rise of a liquid in a capillary; unfortunately it cannot be used with the more viscous materials, for example, lubricating oils. In this method the height of the liquid in the capillary above the level in a larger vessel is measured. The gas in contact with the meniscus affects the capillary constant. For details see textbooks of physical laboratory methods. Table 5 shows the magnitude of surface tension of various liquids.

* Arch f. d. ges. Physiol., **105**, 541, 559 (1904).

TABLE 5

SURFACE TENSION VALUES

	Temperature ° C.	Capillary Constant in $\frac{mg}{mm}$	Capillary Constant in $\frac{dynes}{cm}$	Method
Water	18	7.2–7.5	73.1	Rise in Capillary
Water	18	7 37		Drops
Ethyl Ether	20	1 68–1.71	16.5	Rise in Capillary
Ethyl Alcohol	20	2.24	22.0	"
Acetone	20		23	"
Acetic Acid	20	2 39	23 5	"
n-Butyric Acid	20		26 3	"
Carbon Bisulphide	20	3.42	33.5	"
Glycerine	18	6.65	65	"
Chloroform	16.6	2 73	26	"
Benzol	20	2.97	28 8	"
Hexane A	68.1		13 6	"
Hexane V	82		18.54	"
Kerosene A	25		26 4	"
Kerosene A	0		28 9	"
Kerosene A	50		24 2	"
Paraffin A	54		30 6	Drops
Russian Kerosene	18		30 5	Capillary Waves
American Mineral Oil	18		29 4	"
American Mineral Oil	18		30 4	Rise in Capillary
Olive Oils A	15		35 6	"
Olive Oil	20		35 4	"
Olive Oil	25		34 9	"
Olive Oil	30		34 4	"
Olive Oil	20		34 5	Drops
Mercury	15		436.	In Vacuum

A against air. V against vapor.

The table shows that the surface tension decreases with rise of temperature; mercury is the only liquid (of those given) with a surface tension greater than that of water. The surface tension of mineral oils is near that of fatty oils. Glycerine has nearly the same value as water.

V. SOLIDIFICATION PHENOMENA OF OILS COLD TEST

Fatty oils and mineral oils are mixtures of many components; the liquid and melted portions have a great tendency to supercool. Therefore such mixtures show no sharp freezing point; on cooling, they become more and more viscous, until finally they solidify. The freezing limits of fatty oils depend on the content of solid glycerides; with mineral oils, the paraffin content is important. In narrow tubes capillarity may influence the results; in making the cold test, tubes of standard dimensions should be used.

(*a*) Oils containing water should be shaken with calcium chloride and then filtered; oils containing water are particularly liable to supercooling.

In making the cold test of heavy mineral oils a test should be made with an unheated sample, and another with a sample which has been heated for 10 minutes to 50° and then cooled for 30 minutes in a water bath at 20°.

(*b*) The solid particles separate very slowly and the heat conductivity is poor; it is therefore necessary to cool the samples in the tubes for at least one hour, in fact fatty oils should be cooled from 4 to 10 hours, if solid does not appear. The cooling depends on the width of the tube (generally 15 mm., in some cases, see page 180, 6 mm.).

(*c*) The oils must be cooled to a constant low temperature; this is generally obtained by mixing 1 part of rock salt with 2 parts of ice or snow (– 21°). Other mixtures may be used as follows:

100 Parts of Water (Ice)	Minimum temperature attained
With ice give a temperature of	0°
With 13 parts of potassium nitrate	– 3°
With 13 parts of potassium nitrate and 2 parts of rock salt	– 4°
With 13 parts of potassium nitrate and 3.3 parts of rock salt	– 5°
With 35.8 parts of barium chloride	– 8°
With 22.5 parts of potassium chloride	– 10°
With 20 parts of ammonium chloride	– 14°
With 25 parts of ammonium chloride	– 15°

The freezing mixture is put in the vessel *b* (Fig. 29).

(*d*) The solidification limits are affected by stirring of the oil. If mineral oils are stirred during the change from liquid to solid, solidification is hindered through the destruction of the network of separated paraffin and pitch; on the contrary, stirring of some fatty oils, such as crucifer oils, aids the separation of the solid glycerides. With fatty oils, one sample should be stirred, another left quiet; mixtures of mineral and fatty oils, should be similarly treated. Pure mineral oils must remain undisturbed.

FIG. 28.

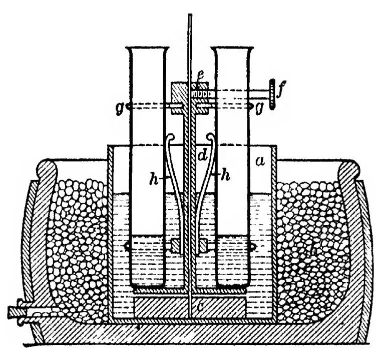


FIG. 29.

(e) A preliminary test should be made with a sample to learn approximately the *temperature of solidification*; oils, which have a great tendency to supercooling, may not solidify in this test. A test tube as shown in Figure 28 should be used.

(f) See Figure 29. Tubes 15 mm. wide are filled to a mark (3 cm. high). *After cooling for one hour to the temperature of the bath, the tubes are inclined and the consistency of the contents noted (still fluid, salve-like or like tallow).*

A salt solution is placed in an enameled vessel (diameter 12 cm.) which itself is put in a larger earthenware pot, wrapped with felt. The freezing mixture is contained in this pot.

For a numerical comparison of fluidity see page 180.

VI. Melting Point, Solidification Point, Dripping Point

These tests are used industrially for the determination of the identity of certain samples, and to determine the purity of the material under examination.

(a) *Melting Point*

The solid fats, paraffin, and ceresine, being complicated mixtures, do not have as sharp melting points as do most chemical individuals. On warming, the material first softens, then becomes translucent, and finally clear when liquid. Since these stages are not easily distinguished, it is customary to note the beginning and end of fusion.

In the capillary tube method, some of the sample is first melted, then cooled to solidify (stirring well to mix). To give a uniform sample, small portions are introduced into a capillary glass tube, closed at one end and about 1 mm. in diameter. The tube thus prepared is allowed to stand at least a day, since otherwise the melting-point may appear too low (fats show a lowering of the melting point under such conditions). The capillary is fastened to a thermometer with a rubber band, the substance being placed at the height of the thermometer bulb. The thermometer is fastened in a test tube 3 cm wide, which is heated in a water bath (beaker). By this arrangement the material may be warmed without superheating. In the neighborhood of the melting point, the temperature is allowed to change only very slowly. The beginning of melting is shown by sintering of the mass on the edges; the end-point is the temperature at which the mass becomes transparent.

For the melting point of pitch, see page 256.

(b) *Solidification Point*

Since fats, paraffin and similar bodies are mixtures which do not have definitely characterized melting points, it is frequently necessary with such materials to determine the solidification point; this is the temperature at which a cooling mass will remain for some time unchanged in temperature, because of the latent heat set free by the change from the liquid to the solid phase (Fig. 30). Three cases may

arise: I. The temperature drops to a point a, remains constant for some time, and then drops again (solidification point is a); II. The temperature drops to the point b, rises rapidly to c, remains constant for some time at c, and then drops again (solidification point at c); III. The temperature drops to the point d, rises rapidly to e and immediately drops again (solidification point at e).

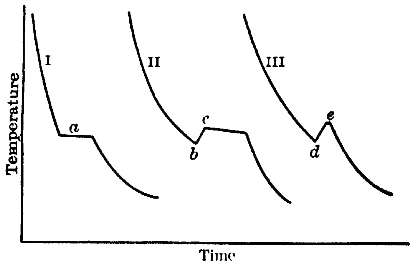


FIG. 30.

The method of Shukoff* is applicable to fats as well as to paraffin. Fig. 31.

30 to 40 grams of the sample are melted in the vessel a. As soon as the temperature has fallen to within 5° of the solidification point the apparatus is shaken strongly and regularly till the contents have become turbid and opaque. Then, without shaking, the temperature is recorded every half minute. As stated above, the point at which the thread remains for some time, or to which it rises, is taken as the solidification temperature.

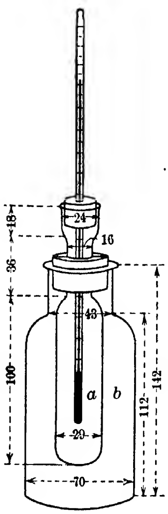


FIG. 31.

For methods which are applicable to paraffin alone see page 245; see also the methods for fats.

(c) *Dripping Point*

Some materials on heating may separate into their component parts; thus a grease may separate into mineral oil and calcium soap instead of melting. Pitch on the other hand because of its dark color may prevent the taking of its melting point. For such materials, as well as for the testing of vaseline, it is customary to determine the temperature at which a portion of the sample will just begin to drip from the bulb of a thermometer around which it has been smeared. For this test, the Ubbelohde method† may be used. Fig. 32.

A thermometer is surrounded by a metal ring b having an opening at c; at the bottom of b is a glass tip e (10 mm. long and having a 3 mm. wide opening) which is filled with material under examination. Some of the sample is pressed into this, taking care to avoid air bubbles.

* Chemiker Zeitung, **25**, Nr. 95 (1901).

† Mitteilungen, **22**, 203 (1904).

Solid substances like paraffin, ceresine, pitch, etc., which might break the apparatus on being inserted, are first melted and poured into the ring resting on a glass plate, the thermometer being inserted before the sample solidifies. The tip is pushed up to the pins *d*. Excess material should be smoothed off the end. The apparatus is then fastened with cork in a 4 cm. wide test tube and heated on a water bath with a rise of 1° per minute; higher melting fats are heated in a paraffin bath. The temperature at which the first arching at the bottom begins is the temperature of flow; the dripping point is the temperature at which the first drop falls. The fat is superheated about 0.5° during this determination; this is, however, only considered in very accurate work.

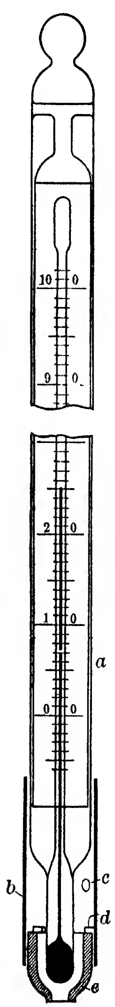


Fig. 32.

VII. Flash Point

Mineral lubricating oils, as well as burning oils, will generate small amounts of combustible vapors even when heated to temperatures which are below the boiling point of the liquid; these vapors will ignite with a flash when a flame is brought near. The temperature of the liquid at which these vapors will ignite, is known as the flash point. The lower the boiling point of the lowest boiling component of the liquid, the lower will be the flash point. The determination of the flash point will give some idea of the volatility of the material and the fire risk involved in handling it. On page 120 are given the flash points of various substances.

1. Pensky-Martens Apparatus

This* is more satisfactory than the open tester because the mode of heating, the method of applying the pilot light, and the observation of the flash are all so much more certain, while with the open tester the collection of the inflammable vapor over the surface of the oil is very easily interfered with by a draft of air. Another advantage of the Pensky apparatus is the fact that the results are easily compared with the values obtained with the Abel tester for more volatile oils. One of its disadvantages is the fact that it detects traces of inflammable vapor which could be disregarded in practice and which would escape unnoticed in the open vessel. See Fig. 33.

The oil is put into the vessel *E* up to the mark *M* (35 mm. high) and heated by the triple burner. The cup *E* is separated from the

* To be obtained from Sommer and Runge, Berlin, W. Friedenau, Bennigsenstrasse, 23.

iron vessel H by a layer of air; the iron vessel is covered by the brass mantel L which carries asbestos paper to prevent loss of heat. Stirring should be begun at 100° (stirrer J). From 120° on, the pilot light Z (a rape oil or gas flame) is made to dip into the air-vapor space by turning the handle G; this flame is dipped every 2° for two seconds, and when the flame begins to lengthen, it is made to approach every degree till the inflammable mixture finally flashes. The temperature read on the thermometer must be corrected for the protruding thread of mercury and for any errors in the scale. Sometimes in flashing, the light will be extinguished; on being relighted and redipped into the air-gas mixture, this need not reflash at once since some time and heating are required to cause the collection of enough inflammable vapor. The observation should be made in subdued light.

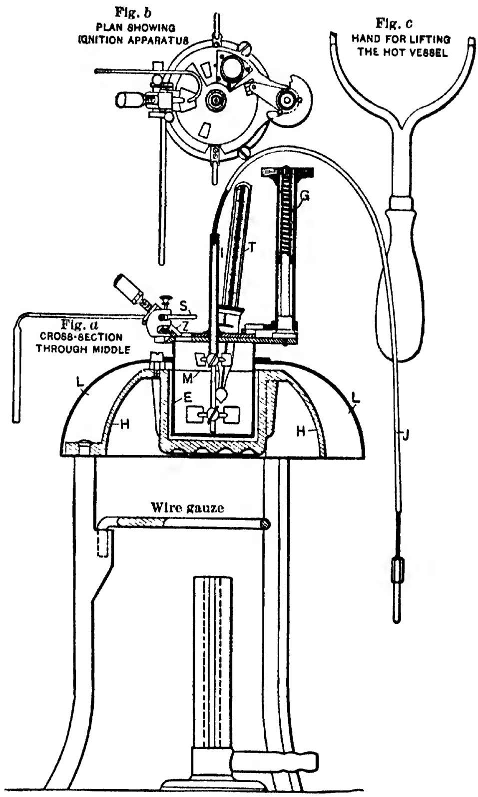


Fig. 33.

With constant stirring the temperature should rise up to 120° at the rate of 6 to 10 degrees per minute; from 20° below the flash point, at the rate of not more than 4 to 6 degrees per minute. This prevents taking too much time for a test and also prevents overheating. If the flash point is under 120° (which is seldom the case with lubricating oils) the stirring should be started at 80° and the pilot dipped from 100° on; to provide for the possibility of the pilot light being extinguished, a safety light S is provided.

The flash point should not vary more than 3 degrees on repetition of the test and generally the differences are less than 2 degrees. Generally only two tests are necessary, but sometimes four are required. The differences may be much greater if pure fatty oil, or a mixture with much

fatty oil, is being tested, because he fats do not decompose evenly, and liberate varying amounts of inflammable gas on repetition. Compounded cylinder oils, generally containing from 5 to 12 per cent of animal oil, which are much used because of their superior lubricating action, generally however show no essential differences on repetition.

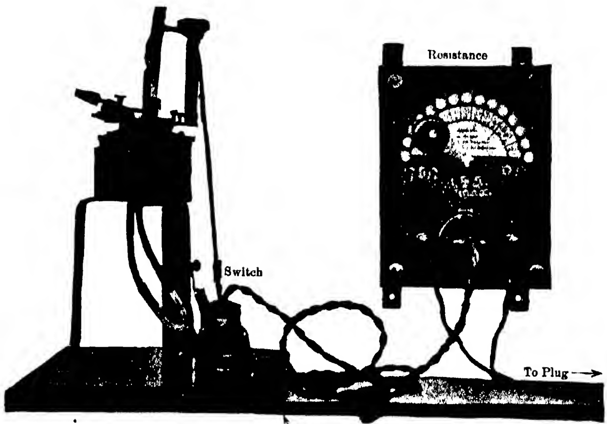


FIG. 34.

The addition of small amounts of easily inflammable oil to a less volatile oil decreases the flash point to a decided degree; the law of mixtures does not apply any more than it did in the case of the viscosity of oil mixtures (page 30). Oil which has been once used for testing should not be used for a repetition, since the flash point may have been raised by the previous loss of more inflammable material. The thermometers should have been standardized while immersed in a bath to the same distance as in the testing.

Oils containing water can be tested in the Pensky apparatus provided that the pilot light is not often extinguished, otherwise they are to be previously dried with calcium chloride and then filtered.

The electric modification* of the Pensky apparatus is shown in Fig. 34. The current is passed through a platinum foil and the resistance box on the wall. With machine oils having a flash point below 200°, a current of 1.5 amperes is used; for cylinder oils flashing up to 320°, 1.7 amperes is advisable. A determination requires 20 to 30 minutes.

* To be obtained from the Vereinigten Fabriken für Laboratoriumsbedarf, Berlin N. W., Scharnhorststrasse.

2. The Abel Tester

This apparatus is used for more volatile materials. See pages 118 and 135 or method of use.

3. The Open Tester

The modification of Marcusson* is an improvement over previous forms of apparatus. There are two forms, one (*a*) used in testing railway lubricating oils, the other (*b*) for the more difficultly inflammable oils (machine and cylinder oils).

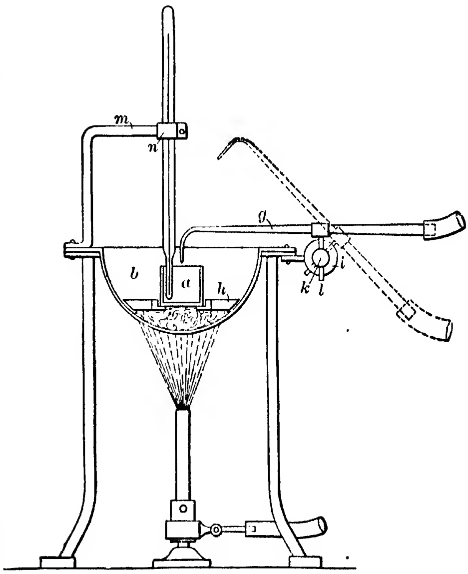


FIG. 35.

(*a*) **For railway oils** (Fig. 35) (according to railway specifications). The porcelain crucible (4 cm. wide, 4 cm. high) is filled with oil up to within 1 cm. from the top; this vessel rests on a frame in the hemispherical (18 cm. wide) sand bath made of sheet iron. The sand is 1.5 cm. deep but the crucible is not imbedded in it. To the side of the sand bath is attached an arrangement *gikl* for bringing a small test flame near the surface of the oil. By heating the oil up to 153° (the average flash point of railway oils) the oil expands and approaches to within 6 mm. of the edge of the crucible. The flame of the blowpipe should be 10 mm. long; as it approaches the hot oil it is bent sideways by the rising vapors, consequently the mechanical arrangement is made to allow the blowpipe tip to drop to within 2 mm. of the edge of the crucible. This determines the distance and position of the flame exactly.

The tripod is best surrounded with asbestos board. Above 100° the temperature should rise slowly, only 3 to 5 degrees per minute at 120°. In testing, the 10 mm. flame is allowed to approach and then remain 4 seconds over the crucible; it then drops back to the dotted position. The flame does not get nearer than 10 mm. to the walls of the crucible so that no overheating can occur

* To be obtained from the Ver. Fabriken f. Laboratoriumsbedarf, Berlin: an electrically heated form is available.

This arrangement is to be used only for the examination of railway oils flashing between 150° and 160°, since for higher flashing oils it is difficult, unless the crucible is completely imbedded in the sand, to raise the temperature at the rate of 3 to 5 degrees per minute.

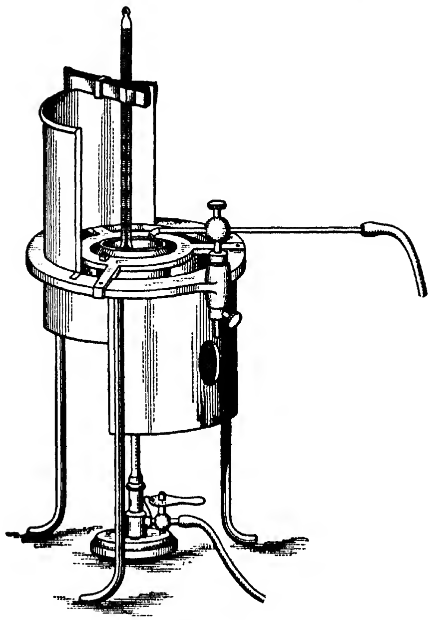


FIG. 36.

(*b*) **For machine and cylinder oils.** (Fig. 36.) A 10 mm. long, horizontal test flame is moved back and forth over the oil in a horizontal plane. The temperature should rise at the rate of 2 to 5 degrees per minute. The crucible is imbedded to the height of the oil level in the sand, the bottom being 2 mm. from the bottom of the shell. The test is made every degree.

This arrangement allows the distance of the crucible from the test flame to be kept constant even when the shell of the sand bath becomes distorted through heating. The crucibles have two marks, 10 and 15 mm. from the top edge. Machine oils are filled up to the upper mark, cylinder oils only to the lower, since otherwise the increase in volume at high temperatures might cause the oil to creep over the edge.

4. The Open and Closed Test Compared

The vapors evolved from mineral oils in the open tester escape more easily and less regularly through drafts of air than is the case with the closed vessel which is open for only a very short time; consequently the flash point in the open vessel will always be higher than for the Pensky apparatus. These differences may range from 5° to 40°. With oils, however, which contain traces of easily inflammable material (naphtha or kerosene) the differences may be much larger, in some cases as much sa 140°. According to some experiments of Holde, the addition of 0.5 per cent of naphtha to an oil, which originally flashed at 180° in the Pensky apparatus and at 200° in the open tester, lowered the flash point in the Pensky apparatus to below 80° while in the open vessel it remained unchanged. At the same time the viscosity of the

oil decreased 8 per cent. Similar results were obtained with other oils. F. Schwartz found that the addition of $\frac{1}{10}$ of one per cent of naphtha to a fat-free cylinder oil reduced the Pensky flash point 100°, an addition of $\frac{1}{30}$ of one per cent of naphtha caused a drop of 70°, while it dropped 20° on adding $\frac{1}{60}$ of one per cent. Flash points of lubricating oils are not comparable unless the apparatus used is known.

VIII. Burning Point (Fire Test)

This is the temperature at which so much vapor is evolved that a continous flame results. The determination is made in connection with the determination of the flash point in the open vessel (Fig. 36). The temperature is raised 2 to 6 degrees per minute up to the burning point. The horizontal flame should approach the oil only 1 to 2 seconds and not touch this, since if the oil is overheated, too low values will be obtained. The burning point is much higher than the flash point (the difference may be 20 to 60 degrees) and in the Pensky apparatus the difference may be greater still (as much as 100 degrees). If it should be decided to determine the flash point in the Pensky apparatus, the burning point can be determined by removing the cover and quickly introducing a thermometer.

IX. Heat Measurements

(a) *Specific Heat Capacity*

In calculating the heating surfaces in tanks in which oils or distillates are to be warmed to separate water, it is necessary to know the quantity of oil, its heat capacity* and the heat conductivity of the heating surface. In the manufacture of paraffin, the size of refrigerating plant is determined by the amount of the paraffin oil, its heat capacity and the heat of solidification (39 calories per gram).

Graefe recommends that the heat capacity be determined by burning in a Hempel bomb-calorimeter definite weights of known standard substances using as the calorimeter liquid, the oil instead of water.† Cellulose [Schleicher and Schüll with a heat of combustion of 4175 calories (Langbein, 4185) per gram] may be used, but not more than 0.41 to 0.43 grams should be taken in order that the temperature rise be not more than 2.5°.

Example. An oil of specific gravity 0.810 and boiling limits 132 to 195° was taken. Cellulose used 0.4085 grams. Temperature rise 2.400°. Heat developed (0.4085) (4175) = 1710 calories. Of this the calorimeter absorbed 377 calories per degree, or for 2.4°, 905 calories. The oil, therefore, absorbed 1710 − 905 = 805 calories for 2.4°, or for each degree rise, 336 calories. The amount of oil used was

* Graefe, Petroleum, **2**, 521 (1907).

† Zeit f. angew. Chem., **13**, 1127, 1259 (1900); also see Petroleum, **8**, 533 (1912).

810 grams. To warm 1 kilogram requires $\frac{336}{0.810}$ or 415 calories for each degree. The specific heat capacity is thus 0.415.

Graefe determined in this manner the following specific heat capacities: Oils from brown-coal tar, solar oil, 0.419, gas oil, 0.416, paraffin oil, (boiling limits 220 to 300°), 0.433; benzol, 0.438; German kerosene, 0.452; heavy paraffin oil, 0.453; crude oil from Wietze, 0.403; American naphtha, 0.487; Galician illuminating oil, 0.473; Russian illuminating oil, 0.451; American illuminating oil, 0.455.

The specific heat capacity may also be determined by an electric resistance method.* The oil is placed in a polished tin-plated calorimeter which in turn rests on porcelain in a similar but somewhat larger vessel. To heat the oil a current is sent through a spiral nickelin wire, this material changing in resistance only slightly with change of temperature. The oil is mechanically stirred; the general scheme

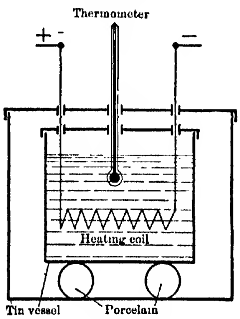


FIG. 37a.

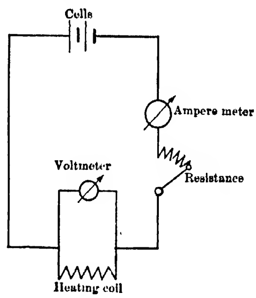


FIG. 37b.

of the apparatus is shown in Figs. 37a and 37b. The specific heat capacity can then be calculated from the amount of oil (m), the water equivalent of the calorimeter (w), the time of heating (z), the temperature rise (t), the strength of current (i), and the resistance of the wire (r). The heat developed in one second is (0.239) $(i)^2$ (r) calories, this being the heat absorbed by the oil. The specific heat capacity can then be calculated from the expression:

$$(m \cdot c + w)\, t = (0.239)\,(i)^2\,(r)\,(z),$$

$$c = (0.239)\left[\frac{(r)\,(z)\,(i)^2}{(m)\,(t)}\right] - \left(\frac{w}{m}\right).$$

The Physikalisch Technische Reichsanstalt determined the heat capacities of some kerosene to be 0.49 to 0.55; of spindle oil, 0.46; of the fractions 201 to 295° from heavy crude oil from Wietze (sp. gr. 0.934), 0.48 to 0.49; of heavy cylinder oils (sp. gr. 0.958 to 0.964), 0.48 to 0.50.

* Kohlrausch, Lehrbuch der praktischen Physik., **1910**, 197.

The specific heat capacity of an oil will be higher the richer it is in hydrogen and, lower, the greater the amounts of carbon and oxygen contained.

Distillates of different specific gravities show at the same temperatures practically the same* heat capacities; the heat capacity however changes considerably with the temperature, for example from 0.48 at 100° to 0.60 at 400°. The increase in the heat capacity is very nearly directly proportional to the change in temperature:

$$C_m = A + \alpha(t^\circ - 100)$$

where C_m is the mean specific heat, A the specific heat at 100°, and α a coefficient which for petroleum products is about 0.000385.

For the heat capacity of petroleum see page 93, of paraffin see page 245, and of fats, see Chapter VI.

(b) *Conduction of Heat*

Thermal conduction by oils plays a part in the transfer of heat in electric transformers which are filled with oil to produce better insulation (see page 159); it is also of importance in the application (see page 230) of graphite-containing lubricating oils.

The thermal conductivity is the amount of heat which in unit time passes through 1 square centimeter area when perpendicular to this the fall in temperature through 1 centimeter is one degree.

In Table 6 are given some values† of the thermal conductivity.

TABLE 6

Material	Conductivity calories/cm. sec. deg.	Material	Conductivity calories/cm. sec. deg.
Kerosene	0 000369	Olive Oil	0 000392
Paraffin Oil	0 000346	Sesame Oil	0.000328
Cylinder Oil	0 000290	Castor Oil	0.000425
Vaseline	0 00044		
Paraffin	0 000473	Water	0.00139
		Glycerine	0 000673
Benzol	0.000333		
Toluol	0 000328	Graphite	0 0117
Xylol	0 000343	Retort Coke	0.0103
Naphthalene	0.00095	Coal	0.00036

* Karawajew, Petroleum, **9**, 1114 (1913).

† Landolt-Bornstein-Roth, Physikalisch-Chemischen Tabellen, 739 to 741.

(c) *Heat of Vaporization*

This is used in the calculation of heating surfaces, size of condensers and quantity of cooling water for the stills, provided that, as is generally the case, this is not worked out on empirical lines. The heat of vaporization may be defined as the amount of heat necessary to change 1 kilogram of liquid at the boiling point into vapor at the same temperature. In calculations it is necessary to include the heat required to raise the temperature of the liquid from room temperature to the boiling point. The sum of these two quantities may be called the "total heat of vaporization."

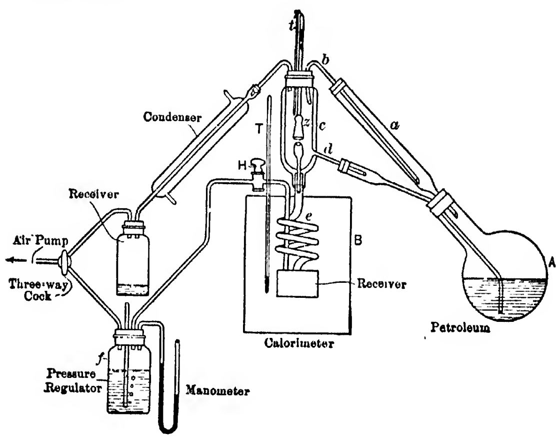


FIG. 38.

For a determination of the heat of vaporization the apparatus of Syniewski* as improved by the Physikalisch-Technische Reichsanstalt may be used. See Fig. 38.

The vapors from the flask *A* pass through *ab* into the double-walled vessel *c* and then under the bell-shaped stopper *z* towards the calorimeter through a metallic coil *e* which is submerged in the water of the calorimeter together with the receiver attached to the coil. The tube *b* is so placed in the wider one *a* that it is surrounded for its entire length by the hot vapors, thus preventing premature condensation. The end of the tube *b* is cut off at an angle and touches the side of *c* to prevent the formation of drops which might allow condensed vapor to be carried over into the calorimeter. Before beginning the calorimetric determination, the condensing apparatus is kept closed by the stopper *z* until all parts of the arrangement, especially the vessel *c*, have been preheated to constant temperature and the liquid condensing in *c*, is flowing uniformly through the tube *d*. If the heat of vaporiza-

* Zeit. f. angew. Chem., **11**, 621 (1898).

tion of a higher boiling fraction is to be determined, the lower boiling portions are allowed to pass into the condenser until the thermometer indicates the initial temperature of the fraction desired. By then raising the stopper z, the vapors pass into the calorimeter, where their heat is given up to about 1200 grams of water. In order to get a sufficient amount of vapor into the calorimeter or the condenser, a slight amount of suction must be applied; for this purpose a water-jet pump is attached to either the condenser or the calorimeter by means of a three-way stop-cock. A pressure regulator f consisting simply of a bottle containing water prevents, in case of irregular working of the pump, too great differences in pressure and allows fixing the maximum difference as that corresponding to the length of tube immersed in the water (never more than the equivalent of a few millimeters of mercury). Before starting a determination, it is advisable to close the cock H and then regulate the pump so that a slow but steady stream of air bubbles issues from the tube of the regulator; the stopper z is then opened, and then immediately, the cock H.

The temperatures of the water and of the vapor are determined by the thermometers T and t. Vapors are passed into the calorimeter from A until the temperature in c has risen about 20°. The evacuation is then stopped, the stopper z closed, the entire distillation apparatus taken from the calorimeter and the amount of distillate determined by weighing the receiver. At the start about 500 c.c. of oil are put into the flask A.

The Physikalisch-Technische Reichsanstalt found the total heat of vaporization of the petroleum products mentioned in the section on heat capacity to range from 130 to 190 gram calories.

The heat of vaporization in general is highest in the lower boiling fractions of any series of hydrocarbons. For example, in the 110 to 130° fraction of Galician petroleum, it is 63.5; in the fraction 170 to 190°, it is only 60; although in the fraction 230 to 250°, the value rises to 62.5, this may, perhaps, be due to partial decomposition of the distillate.

The heat of vaporization may be calculated* from the molecular weight and the average boiling point. Trouton has shown that for pure chemical substances the heat of vaporization (w) multiplied by the molecular weight (M) divided by the absolute boiling point (T) gives a value nearly constant and approximately 20,

$$\frac{(w)\,(M)}{T} = 20.$$

The average molecular weight of an oil is determined by solution in a weighed amount (s) of commercial stearic acid, whose freezing point constant (k) has been determined by a previous experiment with a substance of known molecular weight; a definite weight of oil (o) is taken and the freezing point depression (t) is determined.

$$M = \frac{(o)\,(100)\,(k)}{(s)\,(t)}.$$

* Petrol., **5**, 569 (1910).

The following values were thus determined.

TABLE 7

Lignite tar oils	Specific gravity	Molecular weight
Light crude oil	0.883	113
Heavy crude oil	0.905	158
Gas oil	0 890	158
Light paraffin oil	0.920	190

Similar results* were obtained by means of the vapor density method of Hoffmann.

To determine the mean boiling point, the oil is distilled in the continuous apparatus of Engler (See page 99), the temperatures being recorded at which each successive 10 per cent fraction has passed. The arithmetical mean of these boiling points gives the mean boiling point. For example, with a light crude oil Graefe obtained:

Distillate:	Boiling begins	10	20	30	40	50	60	70	80	90	98 per cent
Temperature:	124°	173°	184°	192°	201°	210°	221°	234°	255°	285°	300°

The mean boiling point is, therefore, 216° C. or 489° Absolute. By the use of Trouton's rule

$$w = \frac{(20)\ (T)}{M} = \frac{(20)\ (489)}{113} = 86.5.$$

To calculate the total heat of vaporization, the heat necessary to raise the oil from room temperature (25°) to the boiling point (216°) must be added. This is (since the sp. heat capacity is 0.43), 0.43 (216 − 25) = 82 calories. The total heat of vaporization is, therefore, 86.5 + 82 = 168.5 calories. Since as much heat is required to warm this oil to the boiling point as is required to evaporate it (and with other oils the ratio is even less satisfactory), the desirability of preheating the oil before distilling is evident.

(d) *Heat of Fusion*

The latent heat of fusion might be defined as the amount of heat necessary to transform one gram of substance, at its melting point, into liquid. It is sometimes used in estimating the amount of heat necessary to melt paraffin, ceresine, tallow and wax, and is used in other important calculations.

* Charitschkoff, Physikalische Untersuchung des Erdoels.

It may be directly determined* in the ice calorimeter. If the melting point of the substance is t_1 (higher than 0°), the specific heat capacities in liquid and solid condition respectively c_2 and c_s, and the amount of ice melted M (80 being the heat of fusion of ice), then the heat of fusion may be calculated as follows:

$$L = \text{latent heat of fusion} = \frac{80M}{m} - c_2t_2 + (c_2 - c_s)t_1.$$

Here m is the weight of the material added at the temperature t_2 to the calorimeter.

It may be indirectly determined by the freezing point depression produced by dissolved substances. This is the method of Van't Hoff.

The heat of fusion of one gram of solvent is equal to 0.002 times the square of the absolute temperature of freezing of the solvent divided by the freezing point constant; the freezing point constant is the depression of freezing point caused by solution of one gram molecular weight of solute in 1000 grams of solvent.

See page 247 for the heat of fusion of paraffin.

(c) *Calorific Value*

Hydrocarbon oils are used directly as fuels in boilers (see fuel oils, page 164) and also as the source of power in internal combustion engines and Diesel motors (see page 162) The calorific value of such oils is the most mportant factor in determining their practical worth.

The calorific value is the number of calories released by the complete combustion of 1 gram of the fuel. A caloric is the amount of heat required to raise 1 gram of water from 15° to 16° C.

The calorific value is determined by burning a weighed amount of fuel in a calor metric bomb with oxygen under 25 atmospheres pressure and determining the heat liberated The method of calculation with explanation of corrections to be applied will be evident from the following discussion.

1. Apparatus and Manipulation

Various types of apparatus† are used for the determination of calorific value. A convenient form, which has been found useful for scientific and industrial investigations, is the Berthelot-Mahler bomb (improved by Kroeker). See Figures 39 and 40.

The calorimeter (Fig. 39) consists of an enameled, or platinum lined, bomb (A), a thermometer graduated to 0.01 degrees (B), a stirrer (C), the actual calorimeter (D) which is surrounded by an insulating vessel of oak or a double-walled vessel of

* Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse und Harze, **24,** 71 (1917). See Kohlrausch, Lehrbuch der praktischen Physik, 211; also Ostwald-Luther, Physikalisch-Chemischen, Messungen, 318.

† See Hinrichsen, Mitteilungen, **30,** 303, 456 (1912); **32,** 291 (1914). Also Hinrichsen, Das Materialprüfungswesen, 388.

copper filled with water (*E*). The bomb (Fig. 40) consists of a nickel-plated steel vessel of about 300 c.c. capacity, fitted with a tightly-fitting screw-on top. There is an opening in the middle of the cover carrying the gas entry and exit tubes. The canal (1) prolonged into a platinum tube (2) leading nearly to the bottom, is used to

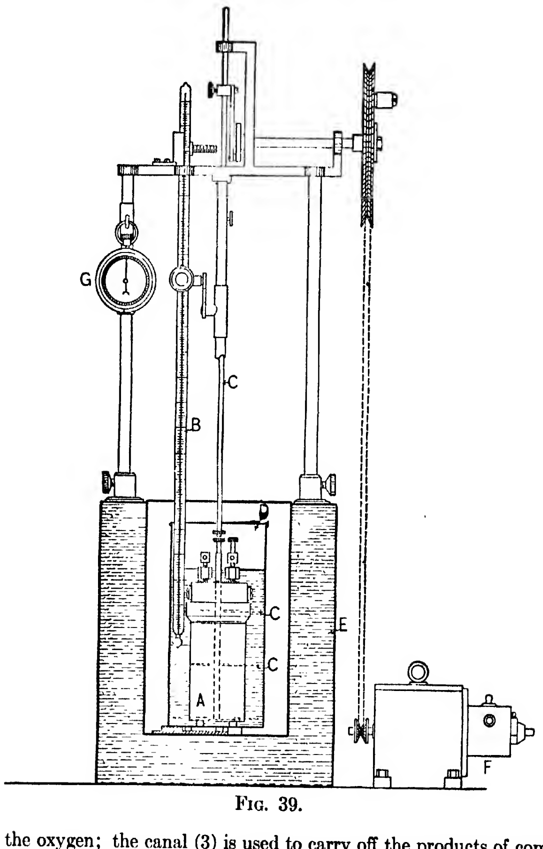


FIG. 39.

introduce the oxygen; the canal (3) is used to carry off the products of combustion. The canals can be closed by the screws 4 and 5. To drive out the air in the bomb the screw (5) is turned and the oxygen entering from a tank displaces the air. Before the bomb is put into the water the side tubes in the top are closed by the screws 6 and 7. The insulated platinum wire (8) leads through the top; the ignition wire is wrapped about the bottom of this and reaches into the platinum cup (9) containing the oil or material under examination, touching both material and the vessel. 10 and 11 are electric binding posts.

An iron wire 5 to 6 cm. long and 0.1 mm. diameter is used for ignition; it is weighed exactly, as it burns to oxide. A platinum wire may be used (0.1 mm. diam-

eter), which obviates the correction applied in the case of the iron, since the platinum melts but does not burn. The bomb and cover must be absolutely dry. 1.0 to 1.5 grams of accurately weighed material are put into the platinum cup, the wire attached, the bomb closed and filled with oxygen under 20 to 25 atmospheres pressure.* The bomb is placed in the calorimeter containing a weighed amount (2000 to 2200 grams) of water near room temperature; this is best as much below room temperature at the beginning as it will be above room temperature at the end. After standing a few minutes the stirrer is started and the temperature read at fixed intervals. When the temperature has become constant or is changing uniformly with the time during 9 minutes (preliminary period), a current of 8 to 10 volts is sent through the wire. The wire ignites the material which in the compressed oxygen burns completely, the temperature rising to a maximum in 2 to 3 minutes (period of combustion). The temperature rise is carefully noted, and after attaining the maximum (as well as during the rise) the temperature is recorded at stated intervals for 9 minutes (period of cooling); the thermometer should be gently tapped during this time.

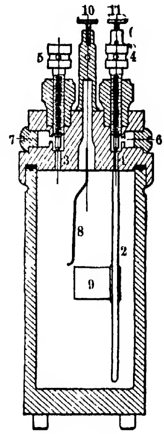


Fig. 40.

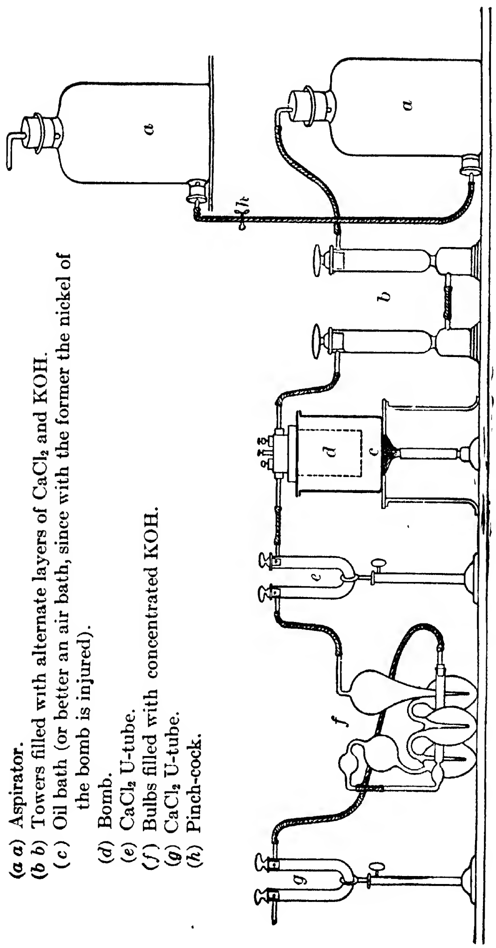
The water formed during the combustion in being cooled to room temperature gives up its heat to the calorimeter; as a consequence, the heat value calculated from the temperature rise will be too large. A quantitative determination of the amount of water formed must be made. To do this, the canal (3) is attached to a weighed calcium chloride tube and after cautiously opening the screw (5) a stream of purified dry air is sent through the canal (2) into the bomb, which should be simultaneously warmed to 105° in an air or oil bath (Fig. 40).

Although it seems to be a very tedious method, it is advisable to determine the water formed during combustion by making a separate analysis of a 0.2 gram sample by the Liebig method of carbon and hydrogen determination; in this procedure, non-volatile oils are weighed in a porcelain boat, but volatile material in closed vessels, which are crushed during the analysis in the combustion tube.

When the bomb is opened after an analysis, the unburned portions of iron wire are collected; this weight is subtracted from the original amount taken for ignition. The amount of sulphuric acid formed from the sulphur in the sample is determined by washing the bomb with hot distilled water, and determining the amount of sulphuric acid by titration, or better still by weighing as barium sulphate.

Very volatile oils, which might evaporate from the platinum container, are weighed in a previously weighed gelatine capsule (the calorific value of which is known; it was 4464 calories in one case). This capsule is burned with the sample, the ignition wire being coiled about it; the heat generated by the capsule must of course be subtracted from the total heat evolved.

* See Zeitschrift für Elektrochemie, **19**, 572 (1913); Chemiker Zeitung, **37**, 1288 (1913).



(*a a*) Aspirator.
(*b b*) Towers filled with alternate layers of $CaCl_2$ and KOH.
(*c*) Oil bath (or better an air bath, since with the former the nickel of the bomb is injured).
(*d*) Bomb.
(*e*) $CaCl_2$ U-tube.
(*f*) Bulbs filled with concentrated KOH.
(*g*) $CaCl_2$ U-tube.
(*h*) Pinch-cock.

Fig. 41.

2. Calculation of Results

(a) *Water equivalent of the calorimeter*

Since the total heat evolved is distributed through bomb, stirrer, calorimeter and thermometer besides the water itself, it is necessary to determine the water equivalent of the apparatus. The easiest way to determine this is to burn a definite weight of a known substance under exactly the same conditions as in the experiment; from the rise in temperature it is then possible to calculate the water equivalent of the apparatus. The standardization material may be either benzoic acid (6325 calories) or cane sugar (3952 calories). The following example will illustrate the method

Benzoic acid	0.8200 gram
Wire for ignition	0.0190
Weight of water in the calorimeter	2000
Observed rise in temperature in the calorimeter	2 201°
Temperature correction (u')	0 009°
Corrected temperature rise	2 210°
Heat developed by the benzoic acid ....(6325)(0.82) =	5186 5 calories
Heat developed by the iron wire...........(1600)(0.019) =	30.4
Total heat developed	5216.9
Heat developed for 1 degree rise in temperature	2360.6
Heat absorbed by the water in the calorimeter	2000.0
Water equivalent of the calorimeter	360.6

(b) *Calculation of the Heat Exchange*

To determine the calorific effect, the water equivalent of the calorimeter plus the water contained, representing the heat capacity of the system, is multiplied by the rise in temperature to find the heat generated by the weighed amount of substance; by calculation then the amount generated by one gram is obtained.

However the observed rise in temperature of the water in the calorimeter must be corrected for the heat exchange with the surroundings by radiation and conduction. This correction (u') is obtained as follows:

u_1 = initial temperature of period of combustion
u_2 = final temperature of period of combustion
Δ_1 = arithmetical mean of 9 temperature increments during the preliminary period
Δ_2 = similar value for the period of cooling
a = a constant of the calorimeter (cooling constant of the entire calorimeter).

Then the calculated external temperature about the calorimeter during the calorimetric measurement is $u_0 = \frac{\Delta_2 \cdot u_1 + \Delta_1 \cdot u_2}{\Delta_1 + \Delta_2}$ and the cooling constant (a) will be $a = \frac{\Delta_1 + \Delta_2}{u_2 - u_1}$.

The difference between the external temperature u_0 and each of the temperatures taken at intervals of one minute is determined; the arithmetical mean of each two neighboring temperatures is determined. The sum of all these arithmetical means (s) multiplied by the cooling constant (a) gives the correction (u') which must be added to the observed rise in temperature (u_2-u_1). This simple method (suggested by Mecklenburg) is illustrated by an example (see Table 8). This gives more accurate results than the much-used graphical method.

In the graphical method, plotting time in minutes as abscissas, the difference in temperature between the "external temperature" (u_0) and observed temperatures during the period of combustion as ordinates giving the u_0 line a value of zero, the difference in area of the two fields (F_2-F_1) is measured (Figure 42). The method is really the same as the above, being inaccurate only because of the difficulty of measuring these areas.

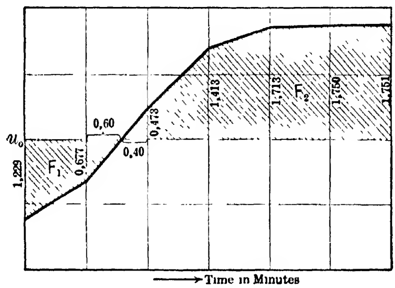


FIG. 42.

(c) *Corrections for Sulphur and Iron*

The rise in temperature during the experiment is $u_2 - u_1 + u'$; this quantity multiplied by the total heat capacity of the calorimeter w gives the heat evolved during combustion. From this value must be subtracted the heat produced by combustion of the iron ignition wire and by sulphur contained in the sample.

The iron burns to the magnetic oxide producing 1600 calories per gram consumed. Usually in the industrial combustion of a fuel, the sulphur escapes from the furnace as the dioxide; in the calorimeter however it produces sulphuric acid. The amount of acid must be determined by titration with 0.1-Normal alkali, in presence of methyl orange; the number of c.c. of alkali multiplied by 3.6 will give the number of calories to be deducted. In very accurate work the amount of sulphuric acid should be determined by weighing as barium sulphate, since during the combustion small amounts of nitric acid may be formed from nitrogen contained in the commercial oxygen used. This correction is usually not important in determining the calorific value, but is absolutely necessary when determining sulphur by combustion with oxygen in a bomb (see page 77).

TABLE 8

	Thermometer Readings Observed	Change of Temperature per minute		
	Preliminary Period			
0	18.209	= 0 002		
1	18 211	0 005		
2	18.216	0 004		
3	18.220	0 007		
4	18.227	0 004		
5	18.231	0 004		
6	18.235	0 006		
7	18 241	0 006		
8	18 247	0 004		
9	u_1 = 18.251			
		Δ_1 = 0.005		
	Period of Combustion			Calculation of the sum of the Arithmetical Means
	u_1 = 18.251		− 19 72 = − 1 478	− 1.057
	20.150		− 19 72 = + 0.421	+ 2.772
	22 080		− 19.72 = + 2 351	+ 5.272
	22 650		− 19.72 = + 2 921	+ 5.960
	22 768		− 19.72 = + 3 039	+ 6 090
	u_2 = 22.780		− 19 72 = + 3.051	20.094
				1 057
				2 | 19 037
	Cooling Period			s = 9.519
0	u_2 = 22.780	0 006		
1	22 774	0 004		
2	22 765	0 010		
3	22.755	0 011		
4	22.744	0.010		
5	22 734	0 011		
6	22 723	0 010		
7	22 713	0 010		
8	22 703	0 010		
9	22.693			
		Δ_2 = 0 010		

Calculated External Temperature $u_0 = \dfrac{\Delta_2 \cdot u_1 + \Delta_1 \cdot u_2}{\Delta_1 + \Delta_2} = 19.72°$ C.

Cooling constant of Apparatus $a = \dfrac{\Delta_1 + \Delta_2}{u_2 - u_1} = 0.003°$ C.

Correction for Heat Exchange $u' = a \cdot s = 0.030°$ C.

The calorific value corrected as above is calculated to one gram of sample. From this value in turn must be subtracted the amount of heat necessary to evaporate the amount of water formed by the com-

bustion of 1 gram of fuel. The amount of water found by the Liebig method multiplied by 6 gives the number of calories to be deducted.

In Table 8 are given the observed temperatures from which the true rise in temperature may be determined as already described.

The following data illustrate the method of calculation.

Weight of Oil. . . . . e			1.0164 grams
Weight of Iron Wire Burned. . . . . . z			0.0139
Weight of Water in Calorimeter . . . a	2000 grams		
Water Equivalent of Calorimeter. . b	328		
Heat Capacity of $a + b$.	2328		
Observed Rise in Temperature. . . . . $u_2 - u_1$		4 529° C.	
Correction u'		0.030	
Corrected Rise $u_2 - u_1 + u'$		4.559° C.	
Heat Evolved $w(u_2 - u_1 + u')$			10613 calories
Deduction for Iron Wire $z(1600)$	22.2		
Deduction for Sulphur* $(n_s)(3.6)$	35.1		
Total deduction			57
Heat of Combustion of 1.0164 grams			10556
Heat of Combustion of 1 gram			10385
Deduction for Water Evaporated (% water) (6)			632
Calorific Value (per gram)			9752 calories

3. Approximate Calorific Effect from Chemical Analysis

If the elementary composition of the fuel is known, it is possible to calculate approximately the calorific value of the material by means of the following empirical expression: †

$$\text{Calorific Value} = 81\,C + 290\left(H - \frac{O}{8}\right) + 25\,S - 6\,F.$$

In this expression, C, H, O and S, represent respectively per cent of carbon, hydrogen, oxygen and sulphur; F is the per cent of hygroscopic water in the oil. The oxygen is determined by difference. With liquid fuel however the agreement with the actual results of the calorimeter is not as good as with solid materials. Mahler‡ always found

* In the analysis for sulphur, 9.77 c.c. of 0.1-normal alkali was used; the Liebig elementary analysis showed 86.3 per cent of C. and 105.5 per cent of water.

† Accepted by the "Verein deutscher Ingenieure;" see also Muspratt, Handbuch der Technische Chemie, 4th edition, **4,** 277; and Hopf, Dampfkessel-und Maschinenbetrieb, **1915,** 313; **1916,** 18, 52.

‡ Compt. rend., **113,** 774, 862 (1892). See also Sherman and Amend, J. Soc. of Chemical Industry, **1912,** 61.

lower values when mineral oils were burned in the bomb apparatus, than were calculated by the formula given. This might be avoided by use of other approximation formulas, but after all actual determination in a bomb is the only certain way to determine the calorific value. Table 9 gives some comparisons.

TABLE 9

Fuel	Calculated by Formula calories	Determined in Calorimeter calories
Fuel Oil.	10630	10100
Gas Oil....	10757	10230
Paraffin Oil	10332	9870

X. Optical Examination

(*a*) **Rotatory Power.** The optical rotation of oils is of value in the direct detection or confirmation of the presence of rosin oil, for the determination of the identity of certain samples and for the investigation of the unsaponifiable portion of wool-fat olein and commercial olein (see pages 522, 448). Mineral oils have a rotatory power of up to 1.2°, at times as much as 3.1°, the rotation being greater the higher the boiling point. Regarding the importance of the small optical activity of petroleum, see page 90.

Rosin oils rotate 30 to 44°, according to Demski-Morawski sometimes 50°, to the right. Of the fatty oils, sesame oil has a rotatory power of + 3.1 to + 9°, because of the strongly dextro-rotary sesamin contained; castor and similar oils show values ranging from + 40.7 to + 43°. The latter contain glycerides of oxyacids with asymmetric carbon atoms; the rosin oils contain optically active terpene radicals. Regarding the optical activity of the turpentine oils see page 317. Mowrah oil has a rotatory power of + 1.1° because of the presence in it of 1.5 per cent of an unsaponifiable body with an optical activity of + 34°.

For a determination of the optical activity, the Laurent half-shadow apparatus and the more accurate and more convenient instrument of Lippich-Landolt are available; the optical chains of the two instruments are shown in Figs. 43 and 44.

A thin plate made of a crystal of potassium bichromate is used as a light filter (in case monochromatic light, as a sodium flame, is used, the plate is unnecessary). Two doubly refracting prisms of Iceland spar serve as the polarizers. In the Laurent apparatus there is a diaphragm, containing a glass plate and a thin quartz plate,

the latter covering one-half the circle. In the Lippich arrangement there are in place of this diaphragm two double prisms, each covering one-third of the circle, leaving the space in the middle free. In both instruments the tube of liquid is placed at *d*, followed by the nicol prisms *e* as analyzers and then three or four small lenses forming the telescope *f* and *g*. The analyzer of the Lippich-Landolt apparatus has attached to it a scale *D* (Fig. 45), the two together being turned by the lever *g*

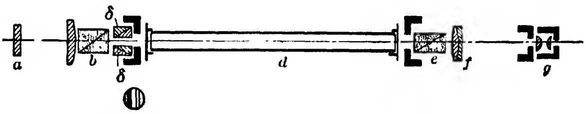


FIG 43.

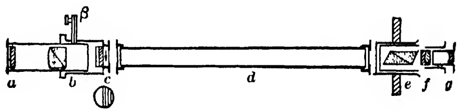


FIG. 44.

(a micrometer screw *m* serving for the final adjustment). The Laurent apparatus can be read to minutes, the Lippich-Landolt to $\frac{1}{100}$ of a degree; but since the adjustment can be made finer in the Lippich-Landolt instrument, the readings with it are much more accurate. In taking the reading it is necessary to determine how many degrees and half degrees have passed the zero point of the vernier; let this be 9° 30′, the zero point of the vernier being between this reading and 10°. It is next necessary to determine at what point two lines, one on the scale and one on the vernier, coincide; this happens to be the twenty-fourth line, representing 24 minutes. The total reading is therefore 9° 54′. As a source of light may be used a Laurent lamp (the Landolt model is better), which accompanies the apparatus, in which a homogeneous yellow light is produced by the vaporization of sodium chloride (fused to avoid decrepitation). Beckmann* has constructed an illuminating gas-oxygen lamp, the flame of which is colored yellow by electrolytically decomposed sodium hydroxide solution; this gives a very bright light, very useful for dark-colored liquids.

1. **Measurement and Filling of the Tubes.** According to the transparency of the liquid, longer or shorter tubes are used; they are measured accurately to $\frac{1}{10}$ mm. In filling and closing, the formation of air bubbles is to be avoided.

2. **Determination of the Zero Point.** This is the position of the nicol prisms at which the field is uniformly illuminated; the zero point must not be confused with the phenomenon resulting from turning the prisms into the less sensitive region where 10 to 15° do not appreciably change the brightness. The point to be looked for is the sudden change from bright to dark. The zero point should be the average of several determinations.

3. **Determination of the Angle of Rotation.** After determination of the zero point the filled tube is put into the apparatus; if now one-half of the field appears darker than the other, the position of the analyzer is determined at which the field appears equally illuminated. The difference between the average of several readings

* Chem. Ztg., **36**, 587 (1912); Ztschr. f. angew. Chem., **25**, 1515 (1912). Biochemisches Zeitschrift, **24**, 423 (1910).

and the zero point previously found gives the angle of rotation. Which direction is dextro and which is lævo must be determined by testing a substance of known rotation. Generally dextro is clockwise.

4. **Determination with Dark Oils.** If the oil is dark colored, so that the sodium light cannot penetrate it, the rotatory power is determined by solution in a clear, inactive solvent, like naphtha, benzol, etc.

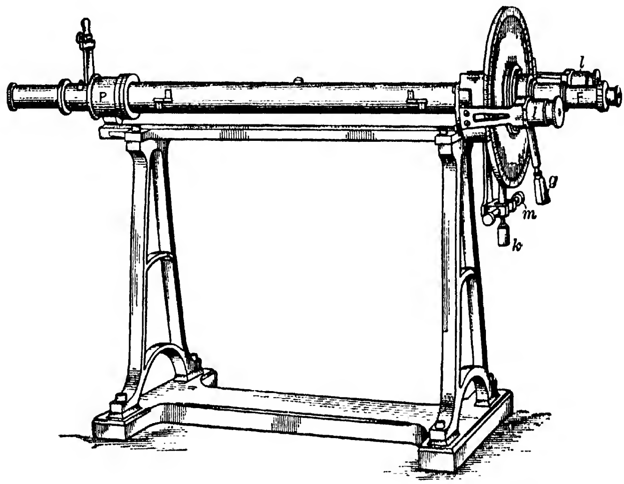


FIG. 45.

5. **General Directions.** To avoid heating the end of the apparatus, the lamp should be at least 10 cm. distant. The determination is best made in a darkened room. The temperature should be determined; the tubes should be left in the apparatus for some time to attain the temperature of the surroundings.

6. **Calculation of the Specific* Rotation.** This is done by the following formulas:

$$\text{I } [\alpha]_D = \frac{\alpha}{(l)\,(d)} \qquad \text{II } [\alpha]_D = \frac{(100)\,(\alpha)}{(l)\,(p)\,(d)} \qquad \text{III } [\alpha]_D = \frac{(100)\,(\alpha)}{(l)\,(c)}$$

where

$[\alpha]_D$ = the specific rotation,
α = the observed angle of rotation,
l = length of the liquid in decimeters,
d = specific gravity,
p = grams of the substance in 100 grams of the solution,
c = grams of substance in 100 c.c. of solution.

Formula I is used for oils in their original condition, formulas II and III when a solution is used. The influence of concentration on the rotatory power of such diluted oils has not yet been determined; the error in the formula can probably be neglected. Generally a four per cent solution is used with formula III.

* Landolt, Optische Drehungsvermögen organischer Substanzen, Braunschweig.

(*b*) **Index of Refraction.** In many cases, for example, to characterize rosin oils, mineral oils, turpentine oils, naphtha, benzols (see these), butter and lard, linseed oil and tung oil, the index of refraction is of value in itself, or in connection with other tests. The determination can be rapidly made with very small quantities of oil.

The Abbe* refractometer (Figs. 46 and 47) the prisms of which are kept at constant temperature by circulating water, as well as the

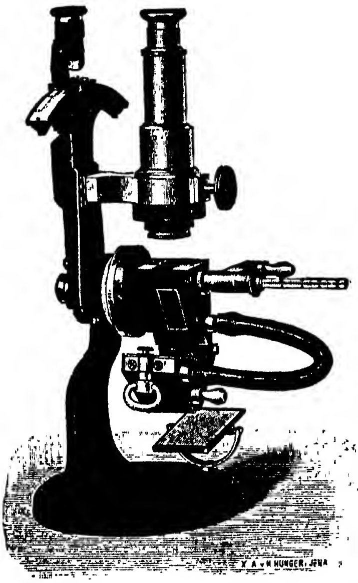


FIG. 46.

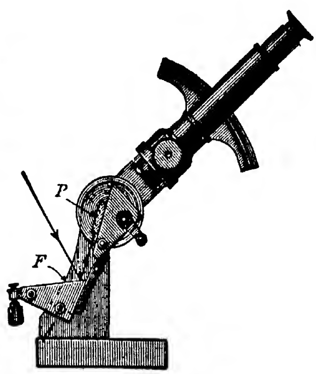


FIG. 47.

butyro-refractometer, especially designed for the examination of butter,* can be used both for liquid and solid fats. Both instruments depend on the observation of the position of the border line of total reflection.

1. **Use of the Abbe Refractometer.** (Figs. 46 and 47.)

The double prism is opened by means of the screw head (see position of Fig. 46) and after carefully cleansing the prisms with cotton and ether, a few drops of the liquid are placed on the horizontal surface of the fixed prism. The prisms are then closed tightly. The telescope is brought to the position shown in Fig. 47. The sector is held firmly and the alidade moved forward from the initial position until the field of vision shows the boundary between light and dark just intersecting

* To be obtained from Zeiss, Jena.

the cross-hairs; the mirror for illumination should have been brought to the proper position and the telescope focused on the cross-hairs. By means of the screw head on the right side of the instrument, the border line should be made as sharp as possible. The index of refraction is then read by means of a lens directly from the scale on the sector. The readings are accurate to about two divisions of the fourth decimal place. The position of the drum on the end of the objective should also be noted in case the dispersion is also to be determined.

TABLE 10

RECALCULATION OF THE SCALE READING INTO THE INDEX OF REFRACTION

Scale division	Index of refraction	Scale division	Index of refraction	Scale division	Index of refraction	Scale division	Index of refraction	Scale division	Index of refraction
0	1.4220	21	1.4385	42	1.4538	63	1.4679	84	1.4807
1	1.4228	22	1.4392	43	1.4545	64	1.4685	85	1.4812
2	1.4236	23	1.4400	44	1.4552	65	1.4691	86	1.4818
3	1.4244	24	1.4408	45	1.4559	66	1.4698	87	1.4824
4	1.4252	25	1.4415	46	1.4566	67	1.4704	88	1.4829
5	1.4260	26	1.4423	47	1.4573	68	1.4710	89	1.4835
6	1.4628	27	1.4430	48	1.4580	69	1.4717	90	1.4840
7	1.4276	28	1.4438	49	1.4587	70	1.4723	91	1.4846
8	1.4284	29	1.4445	50	1.4593	71	1.4729	92	1.4851
9	1.4292	30	1.4452	51	1.4600	72	1.4736	93	1.4857
10	1.4300	31	1.4460	52	1.4607	73	1.4742	94	1.4862
11	1.4308	32	1.4467	53	1.4613	74	1.4748	95	1.4868
12	1.4316	33	1.4474	54	1.4620	75	1.4754	96	1.4873
13	1.4324	34	1.4481	55	1.4626	76	1.4760	97	1.4879
14	1.4331	35	1.4488	56	1.4633	77	1.4766	98	1.4884
15	1.4339	36	1.4495	57	1.4640	78	1.4772	99	1.4890
16	1.4347	37	1.4502	58	1.4646	79	1.4778	100	1.4895
17	1.4354	38	1.4510	59	1.4653	80	1.4783	101	1.4901
18	1.4362	39	1.4517	60	1.4659	81	1.4789	102	1.4906
19	1.4370	40	1.4524	61	1.4666	82	1.4795	103	1.4912
20	1.4377	41	1.4531	62	1.4672	83	1.4801	104	1.4917

The setting and reading of the instrument should be repeated after the drum has been moved through 180° and the mean of the two determinations taken. The reading gives at once the index of refraction n_D for the light of the Fraunhofer line D at the observed temperature of experiment. The temperature correction for oils and fats, paraffin, ceresin, etc., is on the average $-$ 0.0004 (that is, for every degree rise, n_D becomes on the average 0.0004 less). The reading on the drum gives the number z for which the factor "ζ" is to be taken from the dispersion tables going with the instrument. With z larger than 30, "ζ" is to be used in calculations with a negative sign. The table gives two values, A and B, corresponding to the index found so that the dispersion $n_F - n_C = A + (B)$ ("ζ") may be calculated.

Immediately after using, the prisms are to be carefully cleansed with ether and soft linen or cotton. This must be done carefully since the prisms are made of very soft glass. It is even advisable to place a piece of filter paper between the prisms when not in use.

The readings on the scale are correct when water at 18° gives the mean reading

of n_D = 1.3330 or if the normal plate supplied with the instrument gives its proper index.

2. **The butyro-refractometer** (Fig. 48) is very similar to the Abbe refractometer in the construction of its prisms. However the index of refraction is not directly read off, but the border line between light and dark is determined on an empirical ocular scale divided into one hundred divisions. In the examination of butter and lard, etc., the reading is generally stated as so many divisions on the Zeiss butyro-refractometer. The corresponding values for the index of refraction may be taken from Table 10. The observed readings for butter are to be recalculated to 40° in that 0.55 is added to the observed reading for every degree above 40°, or subtracted for every degree under 40°.

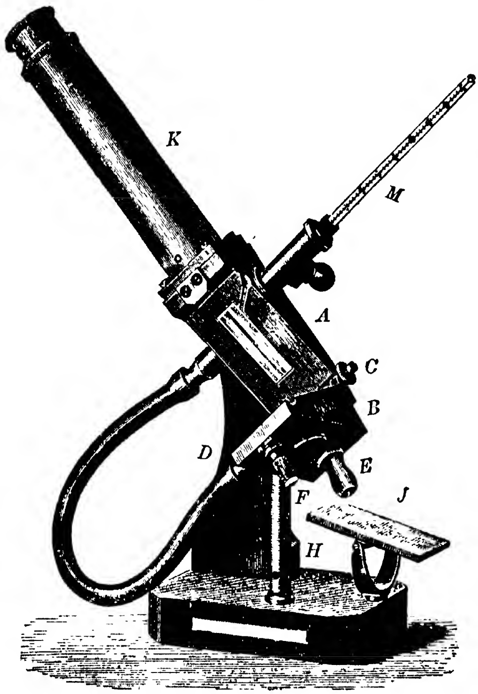


FIG. 48.

Although the instrument is very convenient for the examination of butter, its field of use is limited. Wherever a refractometer is to be used for other substances, the Abbe refractometer is to be preferred since with it the index of refraction may be determined for any value between 1.3 and 1.7.

3. **The Heating Arrangement.** The apparatus shown in Fig. 49 is very convenient for heating the prisms up to higher temperatures with a stream of water at constant temperature.

The water flows from the tank A on the wall through a copper heating spiral to the tank B. Because of the overflow pipes in A and B, the stream of water and the heating is kept very constant. Up to 75°, one spiral is sufficient; for higher temperatures, two spiral coils placed side by side should be used. If a definite temperature is to be maintained for some time, a thermostat with automatic gas or electric regulator should be used. For determinations at 100°, steam is sent through the prisms.

XI. Electrical Tests

One of the electrical tests applied to oils, fats, waxes and solid hydrocarbons is the determination of their conductivity. When pure, these materials are all more or less satisfactory insulators, and are much used as such in the manufacture of cables and in transformers. Since the conductance (or its reciprocal, the resistance) of most pure oils is nearly the same, and since very small amounts of impurities affect the conductance considerably, it is not possible to use this property as a constant for the recognition of oils in mixtures. It is only determined in very special instances, as with transformer oils which must have high insulating power, or in considering the electrical excitation of naphtha (which is made more conducting by addition of soap and therefore less liable to excitation on rubbing with woolen material), or in examining lubricating materials used for sliding contacts.

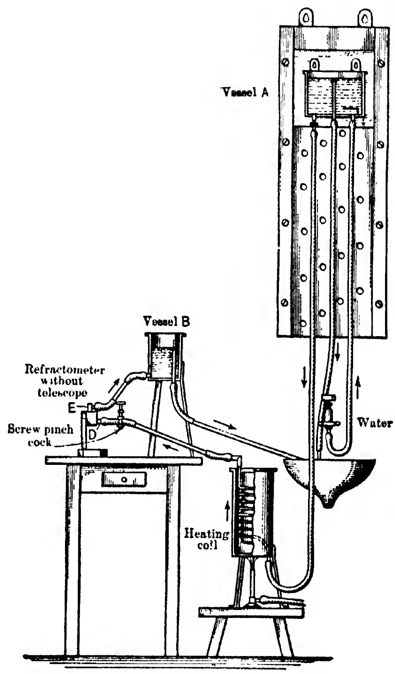


Fig. 49.

The determination of the electrical excitability is necessary only with the very volatile, combustible oils, like benzine, and petroleum ether; these oils are likely to show excitation only when streaming through narrow pipes and under pressure (as when tanks are being filled or emptied) or when agitated with woolen fabrics in naphtha-cleansing establishments. Under such conditions of use they are likely to lead to fires unless proper precautions are taken. Tests are considered under naphtha on page 122.

The dielectric constant is about the same for all hydrocarbon oils, including also paraffin and ceresine, being generally between 1.7 and 2.3; for fatty oils, the dielectric constant is greater, for castor oil being

4.6. The determination of this constant is difficult and is necessary only for electrochemical or electro-technical purposes. It is not used in analytical work.

Conductance

The conductance is the reciprocal of the resistance. It depends upon the accidental form of the body; it is therefore referred to unit dimensions. The specific conductance is the conductance of a body 1 centimeter square and 1 centimeter long. The resistance R of a cylindrical portion of a liquid of cross-section q and length l is

$$R = \frac{(k)\,(l)}{(q)}$$

here k is the specific resistance (the reciprocal of the specific conductance). By Ohm's law $R = \frac{E}{I}$ (E = potential difference, and I = current strength) therefore

$$\text{specific conductance} = \frac{1}{k} = \frac{(l)}{(R)(q)} = \frac{(I)(l)}{(E)(q)}.$$

The determination of conductance depends upon this expression.

The conductance increases with rise in temperature. If an oil is not easily decomposable (naphtha) the conductance will decrease under the influence of an electric current by a convective purification due to the transport of impurities to the poles.

In dealing with solutions of electrolytes, the equivalent conductance is usually determined; it is the conductance of a solution of one gram equivalent weight of solute placed in a vessel with conducting sides one centimeter apart. This equivalent conductance increases with dilution, and decreases on concentration of the solution.

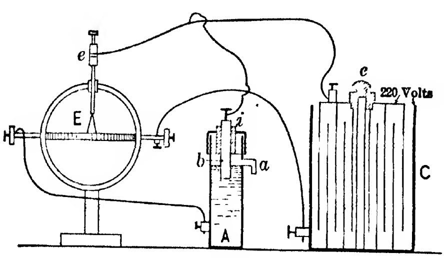


FIG. 50.

But oils are not dissociated; the conductance of an oil which is highly insulating in character cannot be determined by the usual method applied to electrolytes (Wheatstone bridge and alternating current).

In such a case the liquid (oil) is placed in a conductance vessel A; the walls and top (the outer electrode) are insulated by the hard rubber ring i from the cylindrical electrode which dips into the liquid (Fig. 50). The tube a keeps the liquid contained at a definite level. This conductance vessel is connected with a condenser C of known capacity ($C = 10^{-9}$ Farad) and an electroscope, E. The insulated plates of the condenser are charged by the 220 volt circuit. The throw of the leaves of the electroscope is determined in millimeters, and the position of the leaves noted after a fixed time (5 or 10 minutes) has elapsed.

From the observed throw by means of a previously determined empirical curve (Fig. 51), the corresponding voltages E_0 and E_t at the beginning and end of the experiment are determined. The better the conducting power of the liquid, the more rapidly will the leaves drop.

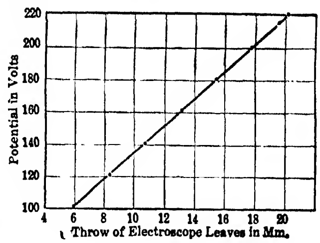


FIG. 51.

If the system were perfectly insulated without the liquid, the conductivity of the liquid would be determined by the expression

$$\frac{2.303\ (C)\left(\log\frac{E_o}{E_t}\right)}{t}$$

which multiplied by the separately determined resistance capacity c would give the specific conductance of the liquid. The vessel and condenser, etc. are not perfect insulators therefore by the same method the conductivity of the vessel without liquid is determined by noting the voltages at beginning and end (E_o' and E_t') as follows:

$$\frac{2.303\ (C)\left(\log\frac{E_o'}{E_t'}\right)}{t}.$$

The specific conductance sought is obtained from the difference of the two expressions

$$\frac{(c)\ (2.303)\ (C)\left(\log\frac{(E_o)(E_t')}{(E_t)(E_o')}\right)}{t}$$

The unknown conductance capacity of the vessel is determined by measuring the resistance of 0.001-normal KCl solution by the usual alternating current, Wheatstone bridge method. If no conductivity vessel with electrodes 1 centimeter square and 1 centimeter apart is available, it is necessary to exactly measure the electrodes and the distance separating them; or better still, the vessel is standardized by means of an electrolyte of known conductance. The resistance measured in ohms at 18° C. is the resistance capacity of the vessel when the specific conductance of the solution

is unity. Since all electrolytes have a smaller conductance, when such an electrolyte is used the resistance determined is multiplied by the specific conductance of the electrolyte used. If the specific conductance is 0.5 and the resistance is 12 ohms, then $c = (0.5)(12) = 6$ ohms.

If, when using the Wheatstone bridge method, a 0.001-normal solution of KCl (specific conductance $= 127.3 \times 10^{-6}$) is placed in the vessel A and a resistance of 100,000 ohms is put in the circuit, the bridge reads 15 to 985, then the resistance of the vessel A must be $\frac{15}{985}$ 100,000 = 1526 ohms. The resistance capacity of the vessel must be

$$c = (1526)(127.3 \times 10^{-6}) = 194 \times 10^{-3}.$$

Example:

The conductance of a sample of naphtha (normal benzine, specific gravity from 0.695 to 705, boiling limits 65 to 95° C.) was determined as follows:

C = capacity of the condenser = 10^{-9} Farad

c = resistance capacity of the vessel A = 0.046

$E_o' = 223$; $E_t' = 147$; $E_o = 225$; $E_t = 141.5$

t = 600 seconds

$$\text{The specific conductance} = \frac{(2.303)(0.046)(10^{-9})}{600} \log \frac{(225)(147)}{(141.5)(223)}$$
$$= 3.5 \times 10^{-15}$$

In carrying out such tests, the conductance vessels must be thoroughly cleansed, so that repeated determinations will give the same values for the specific conductance. Fresh samples must be used in repetitions since under the influence of the 220-volt potential difference (applied for 5 or 10 minutes) a decrease in the conductance will generally occur due to a chemical or convective purification of the liquid. Another precaution which must be taken is to transfer the sample directly from the original container into the conductance vessel, in order that the material may not become electrochemically contaminated; or if this direct transfer is not possible, the intermediate vessel must be repeatedly rinsed with the liquid to be examined. Only by using great care is it possible to obtain results which check.

To determine the conductance of a liquid (like benzol or a mixture of naphtha and alcohol) with less resistance (which therefore is not measurable by the electroscope method because of the rapid drop of the leaves), use is made of the mirror-galvanometer method.

The liquid is placed in a glass measuring vessel A (Kohlrausch) which is connected with the galvanometer BS and a 220-volt current. (Fig. 52.) From Ohm's law $\left(I = \frac{E}{R}\right)$ since E is 220 volts and I is determined by the deflection of the galvanometer, and if c is the resistance capacity of the vessel A, it is possible to calculate the specific conductance from the value of R as follows:

$$\text{Specific conductance} = \frac{c}{R}.$$

The current which corresponds to a deflection of one millimeter on the galvanometer is determined by noting the throw when a resistance of known amount (say 220,000 ohms) is substituted for the measuring vessel and a Weston-cell (E = 1.0187 volts, R = 81 ohms) is used as the source of current. In this case the reading was 534.5 millimeters, and one millimeter is equivalent to

$$\frac{(1.0187)}{(220{,}081)\,(534.5)} = 0.871 \times 10^{-8}.$$

The resistance capacity c = 0.211 of the vessel A is determined by using a liquid of known conductance (0.001-normal KCl solution; this has a specific conductance of 127.3×10^{-6}) by means of the alternating current method with Wheatstone bridge.

The specific conductance is calculated as follows:

$$I = \frac{E}{R}$$

$$R = \frac{c}{\text{specific conductance}}$$

$$I = \frac{(E)\,(\text{specific conductance})}{c}$$

$$\text{specific conductance} = \frac{(I)\,(c)}{E}.$$

For a deflection of one millimeter then the specific conductance will be

$$(0.871 \times 10^{-8})\left(\frac{0.21}{220}\right) = 8.3 \times 10^{-12}.$$

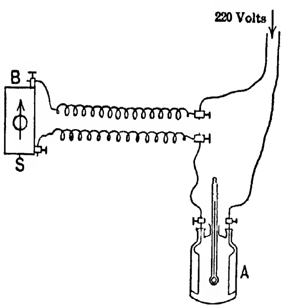


FIG. 52.

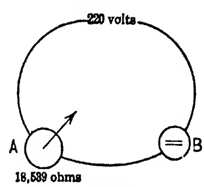


FIG. 53.

The mirror-galvanometer method may be used for values of the specific conductance of from 10^{-9} to 10^{-12} for liquids of greater conductance (from 10^{-7} to 10^{-8}) where the scale of the galvanometer is not large enough, the scheme sketched in Fig. 53 is used.

In a 220-volt circuit is placed a glass measuring vessel (B), used above, and a voltmeter (which has for example a resistance of 18,539 ohms and a scale reading to 150 volts). Since $I = \frac{E}{R}$ for one scale division $I = \frac{1}{18{,}539}$. If the resistance

of the liquid sample to be determined is R_x $\left(\text{since } I = \frac{E}{R_x}\right)$ then for one scale division, $\frac{1}{18{,}539} = \frac{220}{(R_x + 18{,}539)}$ or $R_x = 18{,}539\ (220 - 1) = 4.06 \times 10^6$.

The specific conductance $= \frac{0.21}{4.06 \times 10^6} = 0.52 \times 10^{-7}$.

TABLE 11

SPECIFIC CONDUCTANCES OF VARIOUS MATERIALS

Material	° C.	Specific Conductance
Amorphous Carbon	12	0.25
Graphite	0	$7.9 - 38.5 \times 10^2$
Diamond	15	0.21×10^{-14} to 0.31×10^{-13}
Calcite	273	28×10^{-6}
Mica	20	0.11×10^{-15} to 0.75×10^{-10}
Hard Rubber	20	0.49×10^{-15}
Glass	20	0.20×10^{-13}
Crystalline Sulphur	69	0.254×10^{-15}
Amorphous Sulphur	69	0.562×10^{-10}
Paraffin	18.5	0.34×10^{-18}
Naphtha, C. P.	19	10^{-14} to 10^{-15}
Hexane and Petroleum Ether	19	$< 10^{-18}$
Benzol, C. P.	18	2.5×10^{-12} to 4×10^{-16}
Mineral Lubricating Oil	18	5.8×10^{-11} to 10^{-13}
Anthracene Oil	18	4.7×10^{-8}
Anthracene Oil, free from phenol	18	3.5×10^{-9}
Ethyl Ether, C. P.	18	$10^{-9} \times 10^{-10}$

From Table 11 it will be seen that diamond, mica, crystalline sulphur, hard rubber, paraffin, naphtha, very pure benzol, and purified mineral lubricating oil are insulators. Tar oils, containing phenol, are better conductors; the removal of phenol increases the resistance.

Dielectric Constant

This quantity is not used for analytical distinctions of fats and oils; the methods of measurement need not be here considered. In general the best insulators have the lowest dielectric constants. If that of a vacuum be taken as unity, the dielectric constant of gases is slightly greater than one, while the values for liquids range from 2 to 90. With most inorganic solids, it ranges from 4 to 10; for paraffin it is 1.8 to 2.3, rubber 2.2 to 3, shellac from 3 to 3.7, turpentine oil, benzol and toluol have values of about 2.3, xylol 2.2 to 2.6, kerosene 2, carbon disulphide 2.6, ethyl ether 4.4, ethyl alcohol 26, methyl alcohol 33, formic acid 58, nitrobenzol 36, and water 81.

B. Chemical Tests

I. Acidity

(a) *Free Mineral Acid and Alkali*

Free mineral acid, due to imperfect purification of oils, seldom occurs; alkali sometimes occurs because of alkali soaps added for emulsification, or because the alkaline liquids used in refining have been incompletely washed out. In the latter case the alkaline reaction is immediately detected in the aqueous extract; in the former instance the alkalinity is due to the hydrolytic decomposition of the soaps by the addition of water.

1. Qualitative Detection

About 100 c.c. of oil are shaken with 100 to 200 c.c. of hot distilled water in a separatory funnel. After allowing the oil to settle, the water is run through a moistened filter paper; on adding methyl orange (0.3 gram in 1 liter of water) to the filtrate, the acid will be shown by the appearance of a red color.

Alkali is detected in a similar fashion by adding phenolphthalein to a portion of the filtrate.

2. Quantitative Determination

This is carried out like the qualitative detection but a measured fraction of the water solution is titrated with 0.1-normal acid or alkali.

(b) *Organic Acids*

Organic acids are found in small amounts in nearly all crude oils and petroleum distillates in the form of naphthenic acids, and also in fatty oils to a variable extent, due to the spontaneous decomposition of glycerides. Since these organic acids have different molecular weights, it is usual to report the acidity in terms of the number of milligrams of potassium hydroxide necessary to neutralize one gram of oil; this is the "acid value." Sometimes the acidity is reported as equivalent to a certain amount of oleic acid. In the past acidity has been reported in terms of sulphuric acid anhydride, but this often has lead to misunderstanding about the nature of the acid present as an impurity; the " acid value " or the " oleic acid equivalent " is to be preferred. The relations between these quantities are as follows: 1 per cent of SO_3 $\approx$ an acid value of 14 $\approx$ 7.05 per cent of oleic acid. See tar oils, page 331.

1. **With Light-colored Oils.** The solvent* used is a mixture of 2 parts of benzol and one part of alcohol which has been neutralized with 0.1-normal alkali in the presence of about 2 c.c. of a 2 per cent solution of alkali blue 6*B*; the end point

* Loebell, Chemiker Zeitung, **35**, 276 (1911).

is a distinct red. All apparatus must be rinsed with the solvent before titration. (Fig. 54.) The pipette B has a capacity of 10 c.c. from the cock to the mark; it is fitted by means of a two-holed stopper to a 200-c.c. Erlenmeyer flask, 10 c.c. of oil are run in, the traces washed into the flask with about 75 c.c. of the solvent. The liquid is then titrated with 0.1-normal alcoholic sodium hydroxide (96 per cent alcohol) in the presence of 2 c.c. of alkali blue $6B$ as indicator; the color is observed by transmitted light, it passing from blue to violet to red. This method is applicable with artificially colored oils.

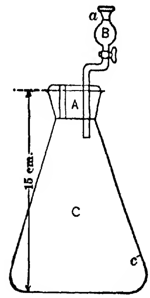


Fig. 54.

If many tests are to be made it may be convenient to graduate a burette in such a fashion that when 10 c.c. of oil are used, and the titration is made with 0.1-normal alkali, it will be possible to read the per cent of oleic acid or the acid value directly from the burette.

If 10 c.c. of oil were used (of specific gravity 0.915) the acidity, calculated as the per cent of oleic acid, is determined, with a burette graduated to cubic centimeters, as follows:

$$\text{acidity} = \frac{\text{(c.c. of 0.1-normal alkali used) (equivalent of oleic acid) (100)}}{\text{amount of oil used in grams}}$$

For example 5.65 grams of oil used 3.2 c.c. of 0.1 normal-alkali (1 c.c. is equivalent to 5.611 milligrams of KOH = 28.2 milligrams of oleic acid). The per cent of oleic acid $= \frac{(3.2)\ (0.0282)\ (100)}{5.65} = 1.6$ per cent. Oils, which contain less than 0.07 per cent of acid (calculated as oleic acid) may be considered as free from acid.

TABLE 12

CORRECTIONS FOR ACIDITY OF DARK MINERAL OILS. PER CENT OLEIC ACID

First extraction	0 106–0 176	0 190	0 204	0 212	0 226	0 233	0 282	0.332	0.381
Correction.	0 035	0 042	0 049	0 056	0.063	0 071	0 078	0 085	0.092
First extraction.	0.437	0.486	0.515	0.543	0 571	0 600	0.627	0.642	0.655
Correction	0.099	0.106	0.113	0.120	0 127	0.134	0.141	0 148	0.155
First extraction.	0.670	0.685	0.698	0.720	0 740	0 762	0 790	0.811	0.853
Correction.	0.162	0.169	0 176	0 183	0.190	0.197	0.204	0.212	0.219
First extraction.	0.895	0.938	0 980	1 022	1 038	1.049	1 063	1.079	1.092
Correction.	0 226	0.233	0.240	0 247	0 259	0.282	0 296	0.317	0.331
First extraction.	1.108	1 120	1 135	1 149	1.162	1 178	1 191	1 206	1.220
Correction.	0 352	0.366	0 388	0 402	0.423	0.437	0.458	0.472	0.493
First extraction.	1 232	1 248	1.262	.	. . . .	.	. . . .	. . . . .	. . . . .
Correction.	0 507	0.528	0.543		. . .	.	. . .	. . . . .	. . . . .

2. **With Dark-colored Oils.** 20 c.c. of oil are shaken in a glass-stoppered measuring flask with 40 c.c. of neutralized alcohol (heating may be necessary with thick

oils). After standing over night, one-half of the alcohol layer is poured off, diluted with neutralized 96 per cent alcohol and titrated with $\frac{N}{10}$ sodium hydroxide (alcoholic, 96 per cent) in the presence of alkali blue 6 *B*. If more than 0.21 per cent of acid (calculated as oleic acid) is present, the oil remaining after pouring off the rest of the alcohol is shaken with a fresh 40 c.c. portion of alcohol and again titrated in the same way. The sum then gives the total acidity. If an error of 0.07 per cent is allowed, instead of making many extractions, by using Table 12, the empirically determined corrections can be applied to the results of the first extraction.

If the acid content of the first extraction is more than 1.4 per cent, (calculated as oleic acid) a second and a third extraction must be made.

3. **With Solid Fats.** Since it is not possible to measure out 10 c.c. of a solid, 5 or 10 grams of sample are dissolved in the neutral alcohol-benzol solvent and then titrated with 0.1-normal alkali.

For the determination of the acidity of oils containing soap, see page 227, and 241; for resins see page 496.

4. **Differentiation of Naphthenic and Fatty Acids.** (*a*) Davidsohn* uses the solubility in water of the alkaline earth salts of the naphthenic acids. The free acids are first separated as alkali soaps by the method of Spitz and Honig (page 197) and then dissolved in water, treated with 10 per cent magnesium chloride solution, boiled, and the precipitate filtered off. The filtrate is evaporated on a water bath and then treated with hydrochloric acid; a white precipitate indicates naphthenic acids.

(*b*) The acids in linseed oil also give magnesium salts which are soluble in water.† But naphthenic acids give, with an equal volume of sulphuric acid and one-half the volume of 40 per cent formalin, formolite derivatives which are not easily soluble in ether, while the transformation products of the fatty acids are soluble in ether. The technical naphthenic acids have an iodine value of from 5.5 to 30.7, a saponification value of from 87 to 157, and a higher specific gravity than fatty acids (0.963 to 0.998). See page 241.

II. Water

Crude oils almost always contain mechanically admixed water, which settles very slowly, especially with thick oils, since the diameter of the drops is often very small. It is also true that water is very slightly soluble in oil.‡ These questions are of considerable importance in the case of transformer oils, since their power of insulation is considerably decreased by the presence of water. Shaking a colorless or light-colored oil with cupric sulphate (anhydrous) cannot be used as a test for water, this not being delicate enough; most paraffin oil or kero-

* Seifensiederzeitung, **36**, Nr. 51/52 (1909).

† Marcusson, Zeitschrift fur angewandte Chemie, **30**, 288 (1917)· Chemische Umschau, **15**, 165 (1908).

‡ Groschuff, Ztschr. f. Electrochemie, **17**, 348 (1911).

sene gives only a faint blue or no color. In order to get a high boiling oil free from water, it is advisable to heat for some time to 120° and then distill in vacuum over an alloy of potassium and sodium (3:1); this last operation is not feasible for transformer oils since these undergo transformation at ordinary temperatures. Groschuff has shown the solubility of water in oil to be as follows (grams of water in 100 grams of solution):

	Benzol	Kerosene	Paraffin oil
20°	0 061	0 006	0 003
50°	0 161	0 024	0 013
94°	..	0.097	0 055

Transformer oil dissolves about 3 to 5 times as much water as pure paraffin oil or kerosene and only about $\frac{1}{3}$ as much as benzol.

(*a*) **Qualitative.** Water may generally be detected in light-colored oils through the cloudiness which is evident after shaking the sample; after heating for some time

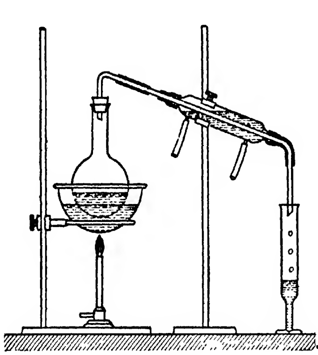


Fig. 55.

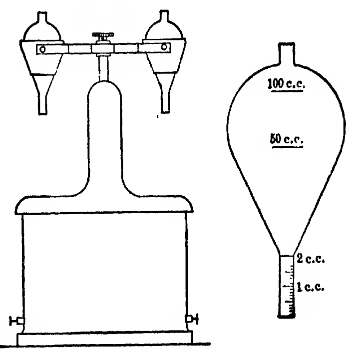


Fig. 56.

on a water bath the cloudiness will disappear and not return on cooling (differing in this respect from paraffin particles, or stearin particles in fatty oils). For a more exact test 3 to 4 c.c. of oil are heated in a test tube (the walls of which have been thoroughly wet by the oil) in a bath of liquid paraffin up to 160° (with steam cylinder oils up to 180°). Oils containing water show a tendency to form emulsions on the walls, foaming and bumping. One or another of these phenomena may fail when only traces of water are present.

(*b*) **Water is Quantitatively Determined as Follows:** 1. About 100 grams of oil (less if much water is present) are distilled from an oil bath with toluol; this toluol should have been previously saturated with water. Pumice is added to avoid bumping. 80 to 90 c.c. are caught in a cylinder constricted to a narrow graduated

tube at the bottom (Hoffman-Marcusson). After washing the inside of the condenser with toluol and loosening any water drops on the side of the cylinder with a stirring rod, the amount of water can be directly read on the graduations (Fig. 55).

2. Industrially it has been found satisfactory* to separate the oil in a centrifugal, using with the thicker oils a steam-heated jacket. R. Albrecht advises the use of a centrifugal making 2000–3000 revolutions per minute, using pear-shaped glass vessels constricted to a graduated tube at the bottom. 50 c.c. of crude oil and 50 c.c. of benzine or benzol are whirled for two minutes and the per cent of water and of dirt read directly from the scale. It must be remembered that both water and mechanically admixed impurities are separated and that for other reasons (as for example, the separation of paraffin) the separation is not sharp.

III. Mechanical Admixtures and Salts

Accidental Mechanical Admixtures (from barrels or containers) can be seen in light-colored oils by inspection; in dark oils they can be detected by pouring through a sieve of $\frac{1}{3}$ mm. mesh and then washing the latter with ether.

(*a*) **Qualitative Test.** By treating the oil with benzol, in which both the oils and asphalt-like bodies are soluble, mechanical admixtures may be detected.

2 c.c. of a well-mixed sample are dissolved in benzol and allowed to stand several hours; by careful inclination of the test tube, the presence of a sediment becomes evident.

(*b*) **Quantitative Determination.** 5 to 10 grams of well-mixed oil are dissolved in 100 to 200 c.c. benzol and allowed to stand over night. The solution is run through a filter dried to constant weight at 105°. The filter is washed free from oil with benzol and then freed from salts by washing with water, the aqueous filtrate giving on evaporation, the quantity of salts. By again drying the filter paper to constant weight at 105°, the amount of undissolved impurities can be determined. Suspended pitch or asphaltic particles, which may be soluble in benzol, are not determined in this way.

The impurities in a large quantity of oil can be determined by filtration through a sieve on which the coarser particles like sand will accumulate. The sieved oil is warmed on a water bath, allowed to stand over night, the main mass of oil decanted and the rest dissolved in benzol and treated as just described. On the paper are collected all impurities, including any sand (which of course would be very harmful in a lubricant).

IV. Ash

The determination of ash is of importance in the examination of many materials. It helps in detecting the presence of salts of naphthenic and sulphur acids which affect the illuminating power of kerosene. It indicates the care taken in the purification of lubricating oils; this is of importance since traces of soap cause the formation of emulsions of the lubricating oil with the condenser water. It helps in the

* Petroleum, **2**, 285 (1906); Chem. Ztg., **33**, 1259 (1909).

examination of pitches, since natural asphalt usually contains considerable ash, while petroleum pitches contain none.

(a) *Ash in Volatile Oils*

About 1 liter of filtered oil (for example, kerosene) is distilled from a retort, the oil being run in through a separatory funnel fastened in the tubulature, until about 20 to 40 c.c. of oil remain. The precipitate on the filter paper is examined qualitatively and quantitatively. The oil is put in a tared platinum dish, the retort washed with naphtha. On evaporation, the residue is incinerated. The ash is given in per cent by weight.

(b) *Ash in Less Volatile Oils and Pitch*

20 to 30 grams of oil are carefully heated in a porcelain crucible or platinum dish with a small flame until only carbonaceous material remains, which is then ashed and the residue weighed. If the carbon does not burn easily, a stream of oxygen is passed over it during the heating.

With light-colored oils the danger that some of the ash will be carried away by the combustion products of rapid burning is overcome as follows:

A 9 cm. filter paper (ash free) is rolled together and dipped into the oil as a wick and is then ignited when saturated; it may be supported by means of a platinum wire wrapped around it and hung over the crucible. In this way most of the oil will burn; this requires 3 to 4 hours. Finally the residue is ashed by direct heating of the dish. Oils containing water, which foam on heating, can be easily ashed in this way. Dark asphaltic oils cannot be burned in this manner since the filter soon carbonizes and the flame is extinguished.

V. Glue and Other Substances Soluble in Water

Animal glue, from imperfectly glued barrels, is sometimes found in oils, though only in traces; alkali soap see page 194), and inorganic salts, because of imperfect purification, also occur.

100 grams of oil are shaken with 100 c.c. of boiling water in an Erlenmeyer flask; after separation of the oily and aqueous layers, an aliquot part of the water solution, which contains the glue and the soap, is filtered and evaporated to dryness on a water bath in a weighed dish (an aliquot part of the aqueous layer is tested with methyl orange for free mineral acid, see page 69). If there is any residue and it appears to be glue from its odor on heating a portion, it is treated with 5 to 8 c.c. of hot absolute alcohol to extract the alkali soaps, the glue being left. The residue is weighed; it gives a characteristic odor on heating on a platinum foil and an aqueous solution gives a precipitate when tannic acid is added. Alcohol also precipitates glue from its water solution.

Sodium sulphate, which occasionally causes a cloudiness in mineral oils, can be detected by the test with barium chloride.

VI. Antifluorescents and Perfumes

Antifluorescents are added to make mineral oils look more like fatty oils (see page 166). The fluorescence or " bloom ' of mineral oils is generally overcome by the addition of nitro-naphthalene; yellow aniline dyes are also used for this purpose but are generally easily recognized by their color. " Debloomed " oils will become dull on standing.

An unpleasant odor is covered by adding traces of oil of citronella or oil of rosemary, or larger amounts of nitrobenzol; the latter is easily recognized by its so-called odor of bitter almonds.

The almost odorless nitro-naphthalene is detected as follows:

(*a*) **Preliminary Tests.** The sample (1 to 2 c.c.) after boiling (1.5 min.) with 2 to 3 c.c. of approximately 2-N alcoholic potassium hydroxide gives a blood red to violet color because of the reduction of the added materials to azo-bodies; in this test the drops clinging to the side of the tube above the liquid are immediately colored red violet, if the glass walls are momentarily heated by waving the flame over them. Blubber oils, free from nitro bodies, give a blood red, all other oils only a brown yellow or a red brown, color.

(*b*) If the preliminary test indicates the presence of nitro-naphthalene, the following method is tried; it depends on the complete reduction of the nitro-naphthalene to naphthylamine by nascent hydrogen.

Several cubic centimeters of oil are reduced in an Erlenmeyer flask by heating for 5 to 10 minutes with tin and hydrochloric acid in the presence of a piece of platinum as a catalyzer; the resultant acid solution will contain, besides unchanged material and stannous chloride, some of the hydrochloride of naphthylamine. This acid solution is carefully separated from the fatty layer, freed from emulsified oil drops by filtration and is then treated with so much sodium or potassium hydroxide in a separatory funnel that the precipitated tin hydroxide is redissolved. After cooling, the solution is extracted with ether to remove the naphthylamine which is recognizable in the free state by its odor; the naphthylamine gives a violet tinge to the ether. From this solution it is obtained, by evaporation of the solvent, in the form of a violet solid of strong odor. Treated with a few drops of hydrochloric acid, a partially insoluble salt is obtained which, on complete evaporation of the acid, gives a clear solution with water; on adding ferric chloride a deep blue precipitate forms; this precipitate, filtered, assumes a purple color, while the filtrate is violet.

VII. Content of Saponifiable and Unsaponifiable Oil

(*a*) *Content of Fatty Oil*

Fatty oils can be detected, by the method of Lux, in liquid or easily melted mineral oils through the formation of soaps on heating the oils with sodium or sodium hydroxide. The Holde and Ruhemann modification is carried out as follows:

3 to 4 c.c. of oil should be heated in a test tube with sodium or its hydroxide for 15 minutes in an oil bath (light-colored oils to 230°, dark oils to 250°). In light oils, ½ per cent and in dark oils, 2 per cent of fatty oil can be detected by the gelatinization or the formation of soap suds (or both phenomena may occur) on cooling the samples. One per cent of fatty oil in cylinder oils can be detected in this way. A blank test with sodium is unnecessary if it is sufficient to detect 1 to 2 per cent of fatty oil. It must be remembered that gelatinization can take place without foaming when rosin or naphthenic acids are present (see page 276). In that case,* the acids are to be separated according to Spitz and Hönig (see page 197) and then characterized by the iodine number, saponification value, solubility in naphtha and by sulphur content.

Quantitative Determination. See page 196.

(b) *Content of Unsaponifiable Oil*

Pure fatty oils and solid fats give, on boiling with N/2 alcoholic potash, soap solutions which remain clear on the addition of water. In the presence of mineral oils, rosin oils and tar oils, oily drops may be seen even before water is added; or on the addition of water, a milky appearance results. It is to be observed that varnishes, free from mineral oil but made from boiled oil, will under this treatment, become cloudy due to the separation of lead and manganese hydroxides from the driers; these precipitates can, however, with some experience be easily distinguished from a cloudiness due to mineral oil. Difficulty from this source can be avoided by treating the material with dilute nitric acid and then washing free from inorganic nitrates.

8 drops of oil are boiled two minutes with 5 c.c. N/2 alcoholic potash in a test tube and then (½ to 15 c.c.) distilled water is added, observing carefully whether a permanent precipitate forms or a cloudiness appears which disappears on adding more water, or if the solution remains clear.

By this method one per cent of mineral lubricating oil can be detected; only in rare cases is the limit of detection 1.25 per cent. Because of the greater solubility of lighter mineral oils in the aqueous-alcoholic soap solution, they cannot be detected with the same accuracy; thus 10 per cent of kerosene may escape detection. For rosin oils the limit is 12 per cent; for lignite tar oils, it is 3 per cent. In this way 0.4 per cent of paraffin† in lard and tallow can be detected. The unsaponifiable alcohols occurring in liquid waxes (sperm oil) are not precipitated on adding water, so that they do not interfere with the detection of mineral oil in such oils.‡

* Schwarz and Marcusson, Mitteilungen, **27,** 17 (1909).

† Dunlop, Analyst, **34,** 524.

‡ Lobry de Bruyn, Chem. Zeit., **17,** 1453 (1893).

VIII. Sulphur, Chlorine and Nitrogen

The customary qualitative and quantitative organic methods may be used but, as a rule, they are not applied industrially since the traces present have no effect on the industrial use of the oil. There are cases of scientific importance where it may be necessary to take them into account.

(*a*) **Qualitative Tests.** 1 to 2 grams of oil with a piece of sodium are heated to redness in a test tube. The residue, in the presence of sulphur, gives a purple violet color with sodium nitroprusside in aqueous solution, a dark stain when placed on a silver coin, and a black precipitate with lead acetate when considerable is present (a brown coloration in the presence of traces).

To test for nitrogen, the aqueous extract of the residue obtained by heating with sodium, after adding a few drops of ferrous and of ferric solutions, is boiled a few moments and then acidified; prussian blue will form but if an excess of concentrated acid is present small amounts of the precipitate may dissolve with a complete disappearance of the color. In the presence of traces of nitrogen instead of a blue precipitate a green solution will form. Quiet standing facilitates the settling of the precipitate but pouring through a small filter will collect it and allow easy detection.

In fats free from nitrogen, chlorine may be found in the ignition residue by solution in nitric acid and precipitation with silver nitrate. If the fat contains nitrogen, 1 gram of fat is gradually added to a platinum or porcelain crucible containing a melted mixture of saltpeter and sodium carbonate (1 : 1), both substances being free from chlorine. After complete combustion of the substance, the residue is allowed to cool, dissolved in water, acidified with nitric acid, nitrous acid expelled by heating and silver nitrate then added.

(*b*) **Quantitative Determination of Nitrogen.** This is only of scientific importance, the methods of Dumas and of Kjeldahl being used.

(*c*) **Quantitative Determination of Sulphur.** 1. This is applicable in all cases but it requires expensive apparatus; the determination is made in a Mahler calorimeter* as follows (see page 49).

1 to 1.5 grams of oil are dropped into the platinum cup of a bomb calorimeter (Fig. 40); the bomb is closed. The bomb is filled with pure oxygen, at 10 atmospheres with naphtha (15 atmospheres with kerosene, 18 for gas oil, 20 for lubricating, the same for crude oil, 25 atmospheres for asphalt, coke or carbon). After electrical ignition (8 volts, 2 amperes), the gases are led into a solution of 2 grams sodium carbonate in 25 c.c. of water After thorough rinsing of the apparatus with distilled water, the solution is evaporated on a water bath to about 50 c.c., aluminum and ferric hydroxides (from the enamel of the bomb and from the ignition wire) precipitating. These are filtered and washed. After acidification with hydrochloric acid and evolution of carbon dioxide, the sulphuric acid is determined by precipitation with barium chloride. Enough oil should be taken to give at least 0.01 gram of barium sulphate.

* Lohmann, Chemiker Zeitung, **35**, 1119 (1911).

2. The method of Rothe has been tested in the Kgl. Materialprüfungsamt with oils containing no naphtha or illuminating oil with satisfactory results.

3 to 4 grams of oil with 1.5 grams of MgO and 30 to 40 c.c. of nitric acid (sp. gr. 1.48) are placed in a 500 c.c. round bottom Jena flask. Hood. After the first violent reaction, the flask is heated gently for 1.5 to 2 hours on a sand-bath, the liquid being kept boiling gently. The excess nitric acid is then evaporated over a free flame and the residue heated till the nitrates begin to decompose. After cooling, 10 c.c. conc. acid are again added. After 15 minutes heating, the mass is evaporated to dryness, keeping the flask in constant motion, then heated with a triple burner until the nitrates are completely decomposed. The residue is generally white; by adding 10 c.c. of hydrochloric acid (sp. gr. 1.124) and heating, it is dissolved and then filtered after diluting with 20 to 30 c.c. of water. In the filtrate, the sulphuric acid is determined by precipitation with barium chloride in the customary manner.

Sulphur may be determined by the Marcusson and Döscher modification* of the Hempel-Graefe method. The substance is burned in an atmosphere of oxygen, the sulphur dioxide being absorbed in NaOH, oxidized by bromine and precipitated as barium sulphate. This method has been used for asphalt but can be used for determining sulphur in oil

In a platinum capsule with 0.5 mm. perforations in the sides (Fig. 57) about 0.3 gram substance is weighed on a little cotton on which has been sprinkled some saltpeter; more niter is added and then covered with cotton. The 7-liter bottle (Fig. 57) is then filled with oxygen and about 100 c.c. of purest sodium hydroxide solution (10 per cent) are added; the capsule is hung on the wire attached to the ground-glass stopper, a thread is fastened to the cotton at one end and to the top of the wire at the other and then ignited, immediately closing the bottle with the slightly greased stopper, this being held down tightly during the combustion. After standing one hour, the reaction product is washed into a beaker, warmed with bromine, cautiously acidified with dilute hydrochloric acid and filtered. Barium chloride is added to the boiling filtrate and the sulphate weighed as usual.

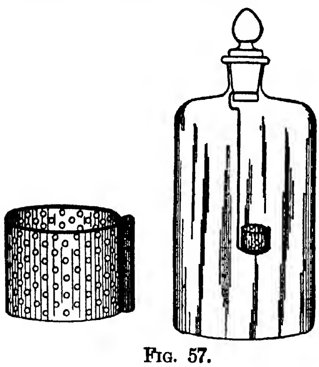


FIG. 57.

The method of Eschka-Rothe† was worked out for the determination of sulphur in coal but is applicable to the substances under consideration. Gaseous oxygen is not required for this method.

* Chem. Ztg., **34,** 417 (1910).

† Oesterr. Ztschr. f. Berg.-u. Hüttenwesen, **22,** 111; Mitteilungen, **9,** 107 (1891).

1 gram of substance is mixed in a platinum crucible with 1.5 grams of a mixture of 2 parts of MgO and 1 part of anhydrous soda of known sulphur content and heated to redness with the crucible in an inclined position; the carbon will be burned in one hour, if the mass is stirred occasionally with a spatula. The residue is treated in a beaker with bromine water and dilute nitric acid and after evaporating the bromine, is filtered. The sulphur is then precipitated as barium sulphate in the filtrate.

(*d*) **Quantitative Determination of Chlorine.** 1 to 2 grams of fat are gradually added to a molten mixture of saltpeter and soda (1 : 1); the mass is then treated as described above for qualitative detection, taking all precautions to make it quantitative. The precipitated silver chloride is weighed.

A method much used in the United States is used for the determination of chlorine in tar oils.

25 to 50 grams of oil are mixed in a platinum dish with 10 grams of pure lime, free from chlorine, and then heated to carbonization at a low temperature on a sand-bath. The residue is dissolved in water, warmed gently and filtered after acidification with nitric acid; the chlorine is then determined as silver chloride in the usual manner.

CHAPTER II

PETROLEUM AND PETROLEUM PRODUCTS

A. Crude Petroleum

I. Occurrence, Refining and Uses

The color of crude petroleum varies considerably; it is generally dark bluish green, dark brown or almost black but may be, as is the case with Pennsylvania oil, light yellow or reddish brown. Crude oil may be as mobile as kerosene or as viscous as tar, and, in the case of high paraffin content, may even have a salve-like consistency.

The crude oil is separated by distillation into (*a*) light and (*b*) heavy naphtha, (*c*) higher boiling illuminating oils and (*d*) still higher boiling lubricating oils and paraffin. By treatment with concentrated sulphuric acid or by filtration through fuller's earth, the crude oil distillates are purified.

Two general types of crude oil may be distinguished: (1) those rich in naphthenes, low in paraffin (from 0 to 1 per cent), containing little benzine (naphtha) as well as very little kerosene but much lubricating oil (as the crude oils from Baku and from Wietze); (2) those containing small amounts of naphthenes, but from 3 to 8 per cent of paraffin and considerable amounts of naphtha, illuminating oils and mobile lubricating oils (examples, Pennsylvania oils, Galician oils, light oils from Hanover and Alsace). There are, however, intermediate varieties. Bustenari (Rumania) oil contains considerable amounts (25 per cent) of naphtha, but only small amounts of paraffin. Mabery states that oils from California, Wyoming and many from Kansas do not fall under this classification.

Argentine* crude oils from the eastern slopes of the Andes resemble Russian oils in high content of naphthenes and lubricating oils (69 to 91 per cent), fair amount of illuminating oils (9 to 13 per cent) and a small amount of paraffin and sulphur (of the latter, 0.07 to 0.16, in some special instances 0.85 per cent); the specific gravity of these oils ranges

* Longobardi, Chem. Ztg., **34**, 1150 (1910).

from 0.898 to 0.957, while the flash point due to low naphtha content may lie between 40° and 90°.

From one Russian oil was obtained 0.2 per cent of naphtha (Baku oil), another sample (Bibi Eibat) gave 4.9 per cent, while a Pennsylvania oil gave 11.5 per cent; a Rumanian (Campina) oil gave 3.4 per cent of naphtha boiling below 120°, with 25 per cent boiling under 150° and 35 to 45 per cent illuminating oil. The residue from distillation in the case of a Rumanian (Bustenari) oil contained 0.5, a Campina oil contained 18 per cent paraffin.

At the present time oil is found in Germany at Wietze in Hanover, and at Obershagen near Peine. Some oil is also found at Pechelbronn in Alsace; the oils of Alsace, which contain considerable paraffin, yield naphtha, illuminating oil, easily solidifying lubricating oils, cleaning oils, gas oils, paraffin and asphalt. Heavy oil from Wietze (sp. gr. over 0.94) contains about 10 per cent of illuminating oil, the rest is lubricating oil and asphalt; light oil from the same source, containing more naphtha and kerosene, also contains 3 per cent of paraffin. Of the German oils, that from Wietze has the highest content of asphalt. The comparisons of the German oils (Table 13) were made by Offermann.*

The world's production† of petroleum for 1919 is shown in Table 14; it is interesting to note that in 1905 about 26,000,000 tons were produced.

During the war the production of Galicia dropped 50 per cent. Holde states that the Rumanian wells, reservoirs and refineries were destroyed, before Rumania was overwhelmed by the German armies, by the British under the direction of their military attaché, Thompson; consequently no oil was produced for some time, but it is said that by August 1918, the Germans were producing and shipping per day about 250 tank-cars of oil.

The products of refining are used in internal combustion engines, as solvents, as illuminating oils, for fuel, for lubrication, in the candle industry, as transformer oils, vaseline, pitch, asphalt, electrode carbon, etc.

* Das nordwest deutsche Erdölvorkommen. F. Vieweg & Sohn, Braunschweig, 1917.

† Petroleum, 9, 746 (1914).

TABLE 13
Oils from Hanover

	Wietze Oil		Oberhagen Oil			Oelheim Oil		
	Heavy	Light	Heavy	Middle	Light	Heavy	Middle	Light
Specific Gravity at 20°.......	0 943 to 0 952	0 880 to 0 882	0 938 to 0 948	0 920 to 0 922	0 917	0 916	0 909	0 849
Flash Point (Open Tester)..	102 to 128	26 to 27	58 to 61	30 to 40	28	71	71	under +10
Engler degree at 20°........	109 5 to 227	5 02 to 5 63	61 3 to 101 1	29 46 to 30 6	23 26	26 6	17 6	1 95
Cold test (U-tube).. ...	−15° 1 to 3 mm.	−3° 1 to 5 mm.	−20° 3 to 13 mm.	−20° 14 to 18 mm	−20° 1 mm.	−20° 20 mm.	−20° 12 mm.	−20° 8 mm.
Asphalt (insoluble in benzine)								
%...	1 1	0 26	0	0	0	0	0	0
Boiling begins °C.	232 to 257	100 to 118	160 to 224	125 to 132	161	211	200	76
Percent distilled*								
at 150°	...	2 to 2 5	. .	1 0	...	....	...	18 5
250°	0 to 2 0	16 5 to 17 5	2 0 to 9 0	13 0	14	5 5	9 0	38 5
275°..........	2 8 to 5 5	22 5 to 23 5	7 5 to 13 5	17 5	19 5	11 0	18 5	43 0
300°.....	8.5 to 12 0	30 0 to 31 5	12 5 to 19 3	22 5	26 0	17 5	22 5	49 5
325°......	14 5 to 19 5	37 5 to 38 5	19 0 to 25 0	28 5	31 5	25.0	34 0	54 0
350°............ . ..	31 5 to 34 0	49 5 to 51 0	31 0 to 40 5	41 0	42 5	35 5	44 5	63 0

* Determined in the custom-house official metal apparatus.

TABLE 14

WORLD'S PRODUCTION* OF CRUDE PETROLEUM IN 1919, BY COUNTRIES
(Figures rounded)

Country	Barrels of 42 U. S. Gallons	Metric tons	Cubic meters	Percentage of total by volume
United States	377,719,000	52,099,000	60,051,000	69
Mexico	87,073,000	12,964,000	13,843,000	16
Russia	25,498,000	3,477,000	4,053,000	5
Dutch East Indies	15,428,000	2,143,000	2,453,000	3
India	8,735,000	1,164,000	1,388,000	2
Rumania	6,614,000	920,000	1,051,000	1
Persia	6,412,000	875,000	1,019,000	1
Poland (Galicia)	6,054,000	829,000	963,000	1
Peru	2,616,000	349,000	416,000	
Japan	2,175,000	290,000	346,000	
Trinidad	1,841,000	256,000	293,000	
Egypt	1,501,100	231,100	239,000	
Argentina	1,183,000	172,000	188,000	
Venezuela	425,000	65,000	68,000	
Alsace	344,000	47,100	55,000	2
Canada	241,000	32,000	38,000	
Germany	234,000	33,000	37,000	
Italy	35,000	4,850	5,500	
Algeria	5,000	800	800	
England	1,900	250	300	
Other Countries	750,000	110,000	119,000	
	544,885,000	76,062,000	86,626,600	100

* Mineral Resources of United States, 1920.

II. Chemical Composition

Crude petroleum* consists mainly of high boiling hydrocarbons, non-aromatic in nature, of which the lighter are insoluble in concentrated sulphuric acid, while the heavier ones are partially soluble; there are also always present bodies containing oxygen and sulphur. Aromatic hydrocarbons (benzol and homologues) are, however, found in some crude oils; California, Texas and Ohio oils, as well as Rumanian petroleum, contain large amounts of heavier, mainly aromatic hydrocarbons. In two Rumanian oils (Campina-Baicoiu, 33 per cent, Bustenari, 48 per cent) heavy components, soluble in fuming sulphuric acid, were found, these being now separated by a process patented by Edeleanu, liquid sulphur dioxide being used. The chemical nature of the viscous lubricating components of crude petroleum has recently become better understood. The polynaphthenes,† occurring in machinery oils, especially in the viscous Russian lubricating oils, are supposed to produce high viscosity; these hydrocarbons do not react with formaldehyde and sulphuric acid to produce solid addition products. Paraffins, olefins, and hydrocarbons of the benzol series (unsaturated naphthenes and terpenes), which react with formaldehyde, are less viscous than polynaphthenes.

The polynaphthenes have the general formula C_nH_{2n-4} and are supposed to be the main components of paraffin oil.‡ The solid hydrocarbons occurring in petroleum, may be either normal saturated bodies, as in paraffin, or isomers of the normal hydrocarbons, as in amorphous, ceresine-like products.

The other components of crude oil (naphtha, illuminating oils, gas oils and paraffin) consist, in the case of Pennsylvania oils, mainly of saturated hydrocarbons of the methane series C_nH_{2n+2}; in the case of Russian oils, naphthenes are the main components, in the investigation of which, Lissenko, Beilstein, Kurbatoff, Wreden, Markownikoff, and others§ took part. Most of the naphthenes are cyclic hydrocar-

* Crude petroleum, as well as the natural gas accompanying it, natural asphalt, mineral pitch, etc., are classed together technically with many substitutes for the latter, under the term bitumen. Recently a classification of bitumens in light of newer knowledge has been given from a scientific standpoint by C. Engler (Petrol., **7**, 400 (1912)); another classification more nearly meeting the technical requirements is given on page 254.

† Marcusson, Chemiker Zeitung, **35**, 729 (1911); **37**, 565 (1913).

‡ Chemiker Zeitung, **37**, 550 (1913); **39**, 613 (1915). Mitteilungen, **33**, **415** (1915).

§ Wischin, Die Naphthene, page 3.

bons (Kishner, Aschan and others) of the type of polymethylenes (pentamethylene, hexamethylene, and methyl hexamethylene), for example

$$CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2.$$

In so far as these are hexamethylene derivatives, they may be considered as hexahydro-benzol or its homologues. The naphthenes do not react with permanganate, only slowly with concentrated sulphuric acid, but are attacked by chlorine, bromine and under certain conditions by dilute nitric acid, though with difficulty, and are much more like the aliphatic than the aromatic hydrocarbons. Concentrated nitric acid forms adipic acid from hexamethylene and glutaric acid from pentamethylene.

Richardson* has found it possible to separate asphaltenes from petroleum by successive treatment with benzine and cold carbon tetrachloride; the oil remaining, after being adsorbed by fuller's earth and extracted with benzine, will, when treated with chloroform, give up to the latter resinous bodies† which are probably cyclic compounds. Asphaltenes and petroleum resins react with formaldehyde and sulphuric acid with the formation of products, soluble with difficulty; by oxidation with permanganate in pyridine solution, resinous, red-brown acids are produced.

The hydrocarbons of the nitrogen- and sulphur-containing Texas oils are mostly members of the C_nH_{2n-2} series, containing a double polymethylene (di-cyclic) ring.‡ Among the German, Galician and Rumanian oils, according to their origin, are found sometimes more derivatives of the methane series, sometimes more members of the naphthene series.

Besides mercaptans and sulphide-like derivatives (Texas and Ohio oils) and asphalt-like resinous bodies containing oxygen and sulphur, hydroquinoline bases are sometimes found accompanying crude oils (in California oils), these being derived from the decomposition of the remains of marine animals (the probable source of petroleum). So far as is known, mercaptans do not occur in American oils.

In the case of a Pennsylvania crude oil, 35 per cent of the part distilling over 200° was soluble in conc. sulphuric acid. This agrees with Mabery's results; Mabery found in the portion boiling over 200° (Pennsylvania, Ohio and Canada oils) saturated hydrocarbons up to

* Proceedings Society of Testing Materials, **6,** (1906).

† Chemiker Zeitung, **39,** 581, 613 (1915).

‡ Mabery, Jour. Amer. Chem. Soc., **23,** 264 (1901).

$C_{20}H_{42}$, but also members of the C_nH_{2n} and of the C_nH_{2n-2} series up to $C_{28}H_{54}$. While the latter* did not solidify at $-10°$, the members of the C_nH_{2n+2} series melted above 50°. Krämer and Spilker found the composition of a Baku lubricating oil, which they carefully purified with concentrated sulphuric acid, to be 87 per cent of carbon, and 13 per cent of hydrogen (corresponding to the formula $C_{20}H_{36}$ or C_nH_{2n-4}; they† assume that two molecules of polymerized decylene $(C_{10}H_{20})_2$ pass into two molecules of $C_{10}H_{22}$ and one of $C_{20}H_{36}$. The portion boiling under 200° contains mostly members of the methane and the naphthene series.

The carbon content of various crude oils varies from 79.5 to 88.7 per cent, the hydrogen content from 9.6 to 14.8, the oxygen content from 0.1 to 6.9, the nitrogen, from 0.02 to 1.1, and the sulphur, from 0.01 to 2.2 per cent. In the following table, elementary analyses of various oils are given:

TABLE 15

Source	C	H	O	S	N	Authority
Pennsylvania	86.06	13.89		0.06		Engler
Oil City, Pa.	85.80	14.04			.	Mabery
Findley, Ohio	84.57	13.62	0.98	0.72	0.11	Mabery
Lima, Ohio	85.00	13.80		0.60	0.68	Rakusin
Beaumont, Texas	85.05	12.30		1.75		Richardson
Ventura, Cal.	84.00	12.70	1.20	0.40	1.70	U. S. G.
Wasatch Range, Utah	86.86	11.89	0.59	0.64	0.02	Mabery and Byerly
Grossny 0.906	86.41	13.00	0.40	0.10	0.07	Charitschkoff
Grossny 0.850	85.95	13.00	0.74	0.14	0.07	Charitschkoff
Tscheleken 0.8736	86.40	12.44	0.377		..	Charitschkoff
Campeni-Parjol	85.29	14.21	. .	0.03	...	Edeleanu and
Bustenari (Prahowa)	86.30	13.32	...	0.18	. .	Tanascu

In Table 16 are recorded some of the properties of the paraffin hydrocarbons known to occur in petroleum.

The following methods are used to separate the different groups of substances occurring in crude petroleum:

1. Acid components (phenols, naphthenic acids) are separated by means of dilute sodium hydroxide.

2. Nitrogen derivatives (homologues of pyridine, etc.) are separated by means of mineral acid (see page 331).

3. Unsaturated hydrocarbons (olefins, acetylenes, terpenes, unsaturated polynaphthenes, etc.) are absorbed in concentrated sulphuric acid, avoiding a rise in temperature. Bromine-addition is also useful

* Amer. Chem. Jour., **28**, 165 (1902).

† Ber. **36**, 645 (1903).

for this purpose. Unsaturated hydrocarbons may also be separated from the lower-boiling mineral oils by treatment with concentrated nitric acid (1.5) at – 10°. Liquid sulphur dioxide has also been used for this separation. Engler has suggested the use of mercuric acetate. See pages 111 and 112.

TABLE 16

Name	Formula	Boiling Point °C.	Melting Point °C.	Specific Gravity (of liquid)
Methane	CH_4	–162	–186	0.415 at (–164°)
Ethane	C_2H_6	–84	–172	0.446 (0°)
Propane	C_3H_8	–38		0.536 (0°)
n-Butane	C_4H_{10}	+1		0.600 (0°)
Trimethyl-methane	$CH(CH_3)_3$	–17		...
n-Pentane	C_5H_{12}	+38	.	0.6263 (17°)
Dimethyl ethyl methane	$(C_3H)_3{\cdot}CH{\cdot}C_2H_5$	+30		0.6385 (14°)
Tetramethyl methane	$C(CH_3)_4$	+9	–20	...
n-Hexane	C_6H_{14}	+71	.	0.663 (17°)
Methyl diethyl methane	$CH_3{\cdot}CH{\cdot}(C_2H_5)_2$	64		0.6765 (20.5°)
Dimethyl propyl methane	$(CH_3)_2\,CH{\cdot}CH_2\,CH_{27}CH_3$	62		0.6766 (0°)
Di-isapropyl	$(CH_3)_2{\cdot}CH{\cdot}CH{\cdot}(CH_3)_2$	58	.	0.668 (17.5°)
Trimethyl ethyl methane	$(CH_3)_3{\cdot}C\,C_2H_5$	49		0.6488 (20°)
Heptane	C_7H_{16}	98.4		0.7006 (0°)
Octane	C_8H_{18}	125.5		0.7188 (0°)
Nonane	C_9H_{20}	149.5	–51	0.7330 (0°)
Decane	$C_{10}H_{22}$	173	–32	0.7456 (0°)
Hendecane	$C_{11}H_{24}$	194.5	–26.5	0.7745
Dodecane	$C_{12}H_{26}$	214	–12	0.7731
Tridecane	$C_{13}H_{28}$ at 760 mm.	234	–6.2	0.7755
Tetradecane	$C_{14}H_{30}$	252.5	+5.5	0.7758
Pentadecane	$C_{15}H_{32}$	270.5	+10	0.7758
Hexadecane	$C_{16}H_{34}$	287.5	+18	0.7754
Heptadecane	$C_{17}H_{36}$	303	+22.5	0.7767
Octadecane	$C_{18}H_{38}$	317	+28	0.7768
Nonadecane	$C_{19}H_{40}$	330	+32	0.7774
Eicosane	$C_{20}H_{42}$	205	+36.7	0.7779 at the melting point
Heneicosane	$C_{21}H_{44}$ at 15 mm.	215	+40.4	0.7783
Docosane	$C_{22}H_{46}$	224.5	+44.4	0.7782
Tricosane	$C_{23}H_{48}$	234	+47.7	0.7785
Tetracosane	$C_{24}H_{50}$	243	+51.1	0.7786
Heptacosane	$C_{27}H_{56}$	270	+59.5	0.7796
Hentriacontane	$C_{31}H_{64}$	302	+68.1	0.7808
Dotricontane	$C_{32}H_{66}$	310	+70.0	0.7810
Pentatriacontane	$C_{35}H_{72}$	331	+74.7	0.7818

4. Aromatic hydrocarbons are separated by the nitration method. Solid nitro-bodies are obtained by treatment of the carefully fractionated portions with nitric acid at normal temperature or slightly higher; Engler* obtained trinitro-bodies by careful treatment of one volume of

* Berichte, 18, 2234 (1885).

the fraction under examination with five volumes of a mixture of two parts of concentrated sulphuric acid and one part of nitric acid (1.45).

5. Unsaturated cyclic hydrocarbons are separated by the formolite reaction (page 110).

6. Solid paraffin hydrocarbons are separated by the method described on page 108. Normal and iso-paraffins are separated by means of chlor-sulphonic acid in which the latter are soluble with the separation of hydrogen chloride.

7. The resinous red to dark brown bodies, which contain less hydrogen and carbon but more oxygen and sulphur than the other components of the oil, can be adsorbed by filtration through bone-black or fuller's earth, the resinous bodies being adsorbed, the rest of the crude oil filtering through; after dissolving the adhering traces of oil by means of naphtha, the resinous portion can be extracted with benzol or chloroform.

8. The asphalt-like bodies which are also resinified and contain even more oxygen and sulphur than the resins just mentioned can be separated as described, or by means of alcohol-ether, naphtha, amyl alcohol, etc., as described on page 104.

III. Formation of Petroleum

This question is of great chemical as well as geological interest. The older hypothesis, by which the petroleum has an inorganic origin, has today, because of the optical rotatory power of the crude oil and for geological reasons, lost favor. Such hypotheses were suggested by Mendelejeff and by Sabatier and Senderens. According to Mendelejeff the petroleum resulted through the action of steam on carbides of iron in the interior of the earth; according to Sabatier and Senderens, hydrogen and acetylenes (resulting from the action of water on alkali and alkaline earth metals, and, on carbides) by contact with metallic bodies, acting as catalyzers, formed aliphatic or cyclic derivatives according to the conditions.

The hypotheses proposed more recently favor in general the formation from organic material. This view is supported by the work of Biot in 1835 on the optical rotatory power of crude oil, to which attention was again drawn by Walden* and by Tschugajeff,† and which has recently been carefully studied and confirmed by Rakusin, by C. Engler and others. Differences of opinion exist only as to whether the petroleum is derived from animal or from vegetable material, or from both.

* Naturwiss. Rundschau, **15,** No. 12–16 (1900).

† Chem. Ztg., **28,** 505 (1904).

C. Engler first showed, by experiment, after Höfer had concluded from geological evidence that the petroleum was derived from marine deposits, that an artificial petroleum could be obtained by the distillation of fats. He carried out his experiments with the fat of marine animals. According to the theory of Engler* the petroleum is formed from the fatty remains of all kinds of life, by decomposition under pressure, after the other accompanying matter (protein substances) has changed by putrefaction into water-soluble nitrogen and sulphur derivatives. The lighter hydrocarbons, resulting from vigorous treatment of fatty acids (adipocere), containing paraffins, ethylenes and naphthenes, are supposed to have polymerized to the higher boiling portions in the course of long geological periods. Engler observed a gradual increase in the specific gravity of his synthetic petroleum on standing, which might be interpreted as a confirmation of the polymerization hypothesis.

According to Engler† naphthenes result by the condensing action of aluminum chloride on ethylenes, also by simple heating of the latter to from 250 to 270°, thus giving a possible explanation for the formation of the naphthenes.

Marcusson ‡ thinks that the higher boiling fractions of petroleum could not have been formed from the more volatile portions, because the former have a greater optical rotatory power than the latter; the opposite view would seem to him the more reasonable one.

According to Stahl§ as well as Krämer and Spilker|| the source of petroleum may be large deposits of diatoms. Potonie has shown,¶ however, that the the material on which the hypothesis was based was really not a diatomaceous earth but really a mixed material, a rock containing animal and vegetable remains and excretions; Potonie considers that petroleum may be a distillation product of this material.** By extraction of a combustible biolith with different solvents, Holde was able to obtain†† as much as 7.7 per cent of fatty, wax-like or colophony-like bodies.

* Ber., **21,** 1816 (1888); **22,** 592 (1889); **26,** 1440 (1893); **30,** 2358 (1897); Jahr. Kgl. preuss. geol. Landesanst., **25,** 350 (1904); Chem. Ztg., **30,** 711 (1906).

† Ber., **42,** 4613 (1909); **46,** 1748 (1913).

‡ Chem. Rev., **12,** 1 (1905).

§ Chem. Ztg., **23,** 15 (1899).

|| Ber., **32,** 2940 (1899); **35,** 1212 (1902).

¶ Jahr. Kgl. press. geol. Landesanst., **25,** No. 2, (1904).

** See in this connection, Monke and Beyschlag, Ztschr. für. prakt. Geologie, **1905,** 13.

†† Mitteilungen, **27,** 1 (1909).

Künkler and Schwedhelm* found in support of Engler's experiments that the calcium salts of fatty acids heated to from 270 to 320° give hydrocarbons like those found in lubricating oil. This is in accordance with the suggestion of Hoppe-Seyler† who pointed out the instability of the fatty acids and the necessity of testing the possibility of the formation of petroleum by the decomposition of calcium and magnesium salts of fatty acids, especially of calcium salts formed by the action of calcium carbonate on the fatty acids, these latter being constituents of adipocere. Künkler and Schwedhelm assume that such salts may be taken as intermediate products in the formation of petroleum by the Engler-Höfer hypothesis. The formation of the lubricating oil portion by polymerization of the more volatile portions according to Engler's theory they consider incorrect since in their own experiments with the decomposition of calcium salts of fatty acids a sufficient amount of high boiling lubricating oils formed; this they considered a sufficient explanation.

The question as to what causes the so very important optical activity of the petroleum is not yet settled. Walden‡ considers that it is to be attributed to vegetable origin, because the vetegable materials are said to have a dextro-rotatory power as does petroleum, while animal materials are laevo-rotatory; but as Engler§ remarks, it is by no means certain that the majority of vegetable fats and oils are dextro-rotatory; moreover, the dextro-rotation of the petroleum may be the sum of a laevo- and an overwhelming dextro-rotation.

Marcusson‖ attributes the optical activity of petroleum to its containing derivatives of cholesterin and phytosterin which are normal components of all fats and of the animal and vegetable plasma; he supports his view experimentally by preparing artificial dextro-rotatory mineral lubricating oil from oleins. He also showed that by distillation of the laevo-rotatory cholesterin it is possible to obtain dextro-rotatory derivatives. The fact that petroleum, as Rakusin¶ has shown by means of the Tschugajeff reaction and Marcusson has shown for petroleum, montan-wax and ichthyol by the Liebermann reaction, gives the tests for cholesterin, is no proof or support of the cholesterin theory, for according to the experiments of Charitschkoff these reactions are also given by synthetic petroleum made from cholesterin-free material.

* Seifensiederzeitung, **1908,** 1285, 1341, etc.

† Naturwiss. Rundschau, **1890,** 82.

‡ Chem. Ztg., **28,** 574 (1904).

§ Chem. Ztg., **30,** 711 (1906).

‖ Chem. Rev., **12,** 1 (1905).

¶ Chem. Ztg., **28,** 505, 574 (1904); also **38,** 950, 1243 (1914).

Petroleum itself is dextro-rotatory; several laevo-rotatory fractions were changed by Engler and his pupils by heating to from 340 to 350° into dextro-bodies, similar to the change brought about by Marcusson with the laevo-cholesterin.

The rotatory power of petroleum is rarely more than one Sacch. degree with a 200 mm. tube. The portions boiling under 200° are generally inactive; the higher boiling fractions show optical activity, with a maximum in the 250 to 300° fraction at 12 to 15 mm. pressure, the activity decreasing with the still higher fractions. The highest value obtained by Engler was + 25°.

In general the Russian, Galician, Rumanian and German oils show a higher optical activity than the North American, particularly the Pennsylvania oils. Since the cholesterin distillates show the highest dextro-rotation in the regions in which petroleum also shows its maximum, this may be considered as a confirmation of the view that cholesterin derivatives are the cause of the activity.

C. Neuberg believed* that the optical activity of the petroleum might be due to its containing decomposition products of protein material. The amino-acids resulting from the protein decomposition might be supposed to have undergone a change into nitrogen-free fatty acids (acetic to caproic acids) which are in part active. This explanation is, however, considered improbable by Marcusson on account of the solubility in water of the products mentioned; these, together with any glycerine, would have been washed away by the water always present. Moreover, because of the low molecular weight, only the little active, low boiling portions of petroleum (naphtha and kerosene) could have been formed from them. Neuberg later showed that the deamidized decomposition products of egg albumen (caproic acid, valerianic acid, etc.) when distilled under pressure, or with addition of lime, together with optically active fat (for example, tri-olein) or with higher fatty acids, gave dextro-rotatory hydrocarbons ($\alpha_D = + 0.5$ to $+ 1.7$). According to Marcusson† these hydrocarbons are not nearly so active as the corresponding high boiling bodies from petroleum; on the other hand, by distilling under pressure the unsaponifiable portions ($\alpha_D = + 15°$) of wool-fat olein (in other words in the presence of cholesterin derivatives) an optically active naphtha ($\alpha_D = + 5.15°$), beginning to boil at 80°, 36 per cent of kerosene fraction (+ 1.50 rotation) and 50 per cent lubricating oil were obtained. He assumes, therefore, that the lighter

* Chem. Ztg., **29**, 1045 (1905); Biochem. Zeitsch., **7**, 199 (1907); Berichte, **30**, 4477 (1907).

† Chem. Ztg., **32**, 30 (1908).

portions of petroleum are formed by a secondary change in the lubricating oil fraction. To this conclusion Engler, who had assumed that the lubricating oils were formed by a polymerization of the lighter portions, assented; he likewise considered the cholesterin derivatives as the main source of the optical rotatory power of the petroleum, while in this connection he attributed to the protein decomposition products a very minor part. The quantitative results would seem to indicate the cholesterin of animal fat or the phytosterin of vegetable fat as the source of the optically active substances.

In confirming the observation of Zaloziecki and Klarfeld of the slight or vanishing optical activity of pale light Galician petroleum and the high activity of the dark heavier oils from the same source, Marcusson points out that the former are, according to the determinations of Rakusin, secondary deposits, and probably, in the light of the filtration theory of Day, resulted from darker oils, the heavier, optically more active components being left behind. In all oils of recent origin, namely in those of Surachany (Caucasus), Montechino (Italy), Valleia (Italy) and Bitkow (Galicia) from 42 to 67 per cent of optically inactive naphtha (boiling below 150°) is present. Although the portion boiling under ordinary pressure below 250° was also shown to be optically inactive, Marcusson does not consider it necessary to assume with Zaloziecki and Klarfeld that terpenes and resins are the source of the optical activity in the dark Galician oils. Since the isomer of cholesterin, phytosterin, is a normal component of the plasma of plants, it may be possible to reconcile the cholesterin theory with that of Witt* and of Krämer and Spilker regarding the formation of petroleum from diatoms and algæ.

Physical Examination

IV. Specific Gravity and Coefficient of Expansion

For significance and determination of these constants see pages 1 and 5.

The specific gravity of crude oil varies between wide limits, 0.703 (Pennsylvania) and 1.016 (Persia). Several values may be interesting: 0.955 for Wietze, 0.882 for Baku, 0.887 for Ohio, 0.870 for East Galicia, California up to 1.01, Texas 0.90 to 0.97, Canada generally 0.80 to 0.90, Pennsylvania 0.703 to 0.880.

A low specific gravity indicates high content of naphtha and illuminating oil, a greater density means higher boiling fractions and asphalt.

* Prometheus, 1894, 349, 365.

Even if the specific gravity is of little value in determining the origin of an oil, it can be used for classification of oils from a known source and is used technically as a test for identity and for comparison, since the specific gravity determination gives the simplest test of uniformity in the source of oil supply.

The coefficient of expansion is of importance in recalculating the specific gravity from one temperature to the normal of 15° or 20°, as well as in considering the expansion of the oil in tanks or stills. The coefficient of expansion is 0.000,840 for Pennsylvania oils of density 0.816, with Russian oils of density 0.882 it is 0.000,817, with Wietze oil of density 0.955, 0.000,647; α is larger with oils of lower specific gravity. The change of the specific gravity for 1° is obtained by multiplication of the specific gravity by the coefficient of expansion.

TABLE 17

Source	Specific gravity	$\alpha \times 1{,}000{,}000$
Canada	0 828	843
Schwabweiler	0 829	843
Schwabweiler	0 861	858
West Galicia	0 885	775
Walachei	0 901	748

TABLE 18

COEFFICIENT OF EXPANSION OF RUMANIAN OILS

Source	Specific gravity at 15°	α	Change of specific gravity for 1°
Baicoi	0 8310	0.000,864	0 000,7173
Campina	0 8375	0 000,823	0 000,6837
Bustenari (Telega)	0 8540	0.000,834	0 000,7116
Moreni	0.8690	0 000,850	0 000,7380
Tintea	0.9095	0 000,735	0 000,6676

V. SPECIFIC HEAT CAPACITY

For significance and determination of this constant see page 43. Mabery and Goldstein* have determined the heat capacities of various samples of petroleum.

* Amer. Chem. Journal, **28**, 69 (1902).

TABLE 19

Source	Specific gravity	Specific Heat Capacity
California	0.9600	0.3980
Texas	0.9466	0 4009
Texas (Lucas Well)	0.9200	0.4315
Russia	0.9079	0.4355
Wyoming	0 8816	0 4323
Japan	0 8622	0 4532
Berea grit	0 7939	0 4690
Pennsylvania	0 8095	0.5000

The specific heat capacity of petroleum is larger with oils of lower specific gravity.

VI. Heat of Vaporization

For the determination and significance of this constant see page 46. In Table 20 are given the values for the heat of vaporization of various components of crude oil.*

TABLE 20

	Boiling Point	Temperature of Vapor	Heat of Vaporization
Heptane	98	98	74
Hexane	68	68	79
Decane	173	159	61
Hexamethylene	81	69	87
Naphtha (0 743)			79
Naphtha (boiling at 250°)			75
Russian Kerosene			75

* Engler-Höfer, Vol. I, 155.

VII. Fuel Value

For the determination and significance of this constant see page 49. In Table 21 are given some values* for crude oils from different sources.

TABLE 21

Material	Origin	Specific gravity at 0°	Fuel Value	
			Calories per gram	B.T.U. per pound
Heavy Oil.	West Virginia	0 873	10,180	18,324
Light Oil . .	West Virginia .	0 841	10,223	18,400
Heavy Oil. .	Pennsylvania	0 886	10,672	19,210
Light Oil .	Pennsylvania	0.816	9,963	17,933
Crude Oil......	Pechelbronn	0 912	9,708	17,475
Crude Oil......	East Galicia	0 870	10,005	18,009
Crude Oil......	West Galicia .	0 885	10,231	18,415
Crude Oil......	Balachany . .	0 882	11,070	19,926
Light Oil. .	Baku . .	0 884	11,460	20,625
Heavy Oil.	Baku . ..	0.938	10,800	19,440
Residue	Baku	0 928	10,700	19,260
Heavy Oil. .	Ohio..... ..	0 887	10,399	18,720
Crude Oil.....	Java...... . ..	0 827	9,593	17,267
Crude Oil.....	Java..........	0 923	10,831	19,500

VIII. Inflammability (Fire Risk)

Depending upon the temperature of the flash point, this determination is made according to page 38 or page 135.

The flash point is the temperature at which so much vapor escapes from an open vessel that the mixture thus formed with the air will ignite when a pilot light is moved over the surface of the oil; in the Pensky apparatus, it is the temperature at which in a closed vessel, so much vapor has mixed with the air of the container. that an inflammable gas mixture is formed.

Crude oil flashes generally near 0°, oils rich in naphtha (Java, American, etc.) much lower, those free from naphtha (heavy Hanover) may not flash below 70°. The flash point is determined by means of the Abel or the Pensky apparatus (pages 38 and 135).† The Prussian police

* Engler-Höfer, Vol. I, 161.

† See in this connection, Zentralblatt für das Deutsche Reich, **1898**, 281, 282.

regulations classify inflammable mineral oils into three grades according to their fire risk:

Class I with a flash point under 21° C.
Class II with a flash point from 21° to 65° C.
Class III with a flash point from 65° to 140° C.

IX. Optical Properties

The optical properties can only be determined in sufficiently light-colored oils or oils clarified through proper filtration, which operation, however, removes some of the components of the oil. The rotatory power and refractive index could be determined, but as yet no industrial significance is attached to the test. These tests are described on page 57. The connection between optical activity and the formation of petroleum has already been considered (page 90). It is possible that such determinations may at times give information regarding the source of the oil.

Chemical Tests

X. Water Content

Since petroleum occurs associated with salt water, the oil nearly always contains water; this contained water causes foaming during the distillation of the oil. For the determination of water see page 72.

XI. Mechanical Impurities

Petroleum will at times be found to contain sand, salts, particles of wood, etc.; they are separated as described on page 73.

XII. Determination of the Amounts of the Different Fractions on Distillation

The method of procedure in distilling an oil depends on conditions; for factory analysis, the method of procedure must be similar to the general method of manufacturing and it is to be varied according to the circumstances. In technical and commercial analysis it is highly desirable that methods of procedure and the apparatus be uniform in order to facilitate comparisons of samples.

1. **For the Manufacturer.** The arrangements for laboratory distillation are different depending on the needs of the factory, the source of raw material and the method of distillation (steam or cracking process). The height of the dephlegmators has a decided effect on the

relative yield of naphtha, kerosene, etc. How little a laboratory distillation may correspond to the yield in a refinery has been shown by Vieth (Table 22).

TABLE 22

Crude oil from	Distillates	In laboratory, per cent	In refinery, per cent
Bradford, Pa......	Naphtha	10 5	10
	Kerosene	63 5	80
	Paraffin oil	17 0	2
	Coke and loss	9 0	6
Rumania........ ...	Naphtha.	15 0	10
	Kerosene	45.0	60

It is customary to distill in a laboratory experiment about 0.5 to 1.0 kilogram of oil from a glass or metal retort, using at first a water condenser and later cooling with air, catching fractions between definite limits (up to 150° for naphtha, to 300° illuminating oil, etc.), measuring or weighing these and determining their properties. Those portions boiling over 300° (lubricating oils) are distilled, as in the refinery,

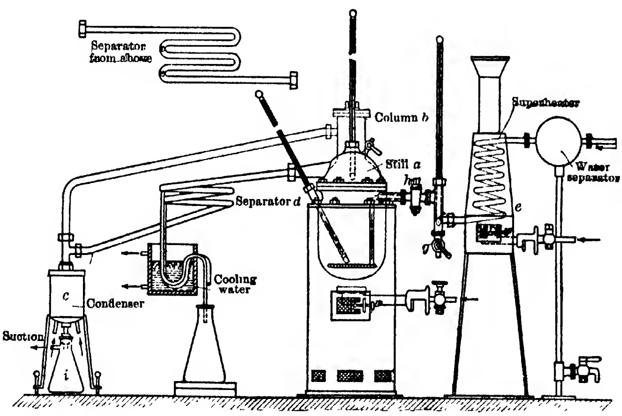


FIG. 58.

with superheated steam and, at times, as for example with heavy German oils, also under a pressure of only 300 to 400 millimeters. Some oils would undergo a deepseated transformation if heated directly, with the formation of foul smelling products. In dis-

tilling with steam there is frequently used the Engler method of separation by air cooling, which separates the distillate into light and heavy lubricating oil fractions through the difference in the ease of condensation. Such an arrangement for distilling on a laboratory scale with either superheated steam or with partial vacuum is shown in Fig. 58.

The crude oil is warmed, if necessary, on a water bath with granular calcium chloride (or with a solid mixture obtained by fusing together 1 part by weight of calcium chloride and 4 parts of sodium chloride) to remove water and is then filtered; if it contains considerable naphtha, it is better to work at room temperature to avoid volatilization of this component. 1 to 2 kilograms of dry oil are distilled with the column attached to the still; a water condenser should be used until the temperature of the vapors reaches 280°. The column is filled with metallic grids resting on rings. The fraction up to 150° is known as naphtha, between 150 and 280° as kerosene. The column *b* and the condenser are then detached and the lower dome attached to the separator *d* and the condenser *c*. Steam from a Landolt generator or from any available source is passed through a superheater (a copper coil in a galvanized iron jacket) until on escaping from *g* only a slight mist is seen. By opening the cock *h* the steam is carefully passed into the still, the entry tube extending nearly to the bottom. The mixed oil vapors and steam pass through the separator *d*. The steam should be superheated from 150° to 250° and at times with cylinder oils even more. The heaviest oils condense in the first separator tube, lighter oils in the second, etc.; the most volatile are condensed by the cooler *c*, and, thus separated from the more valuable lubricating oils, are caught in the receiver *i*. In distilling with both steam and diminished pressure, the apparatus of Fig. 59 is available.

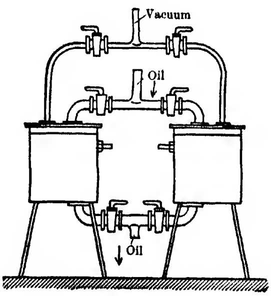


Fig. 59.

The oil vapors are rapidly removed from the decomposing action of the hot walls of the still by a rapid current of steam; the entire apparatus is covered with asbestos to prevent loss of heat by convection and radiation. The receivers are changed when a marked change in the consistence becomes evident.

In place of the apparatus described, for most laboratories a simpler arrangement (Fig. 60) with a copper or glass distilling flask, vertical copper separators with three outlets, corresponding to the figures of Engler* will be sufficient when working without a vacuum.

The cork stoppers are made tight by a paste made of linseed meal and water.

The fractions of approximately the same viscosity and the same specific gravity are collected together in the order of their boiling limits as naphtha, illuminating oil, gas oil, spindle oil, machine oil; these are then treated with 1 to 8 per cent of conc. sulphuric acid to remove bad-smelling unsaturated compounds as well as to lighten the color.

In washing the mineral oils refined with sulphuric acid, emulsions are likely to form when the aqueous solution of alkali is added and these are broken up only with

* Verhandlungen des Vereins für Gewerbefleiss, **1887**, 683.

great difficulty in the separatory funnels which are generally used. The washings must be made hot and with vigorous shaking, in order that the oil may be completely separated from the wash liquid; this is easily done in the apparatus of Fig. 61. It consists of the vessel *a*, which is fitted with a stop-cock *d* (the second *d'* may be used to separate the small amounts of oil passing through the upper cock), an

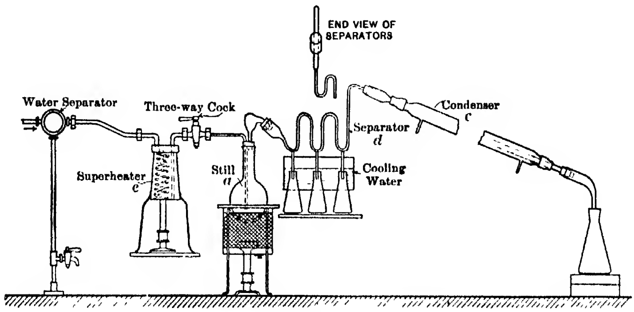


FIG. 60.

aluminum or well-annealed glass coil *b* and the tube *c* for stirring the liquid by means of a stream of air. In order to also refine with acid in this apparatus, another cock is to be attached at the bottom. The refined oils are dried by passing a stream of air through the strongly heated oil.

After refining, the fractions are examined for external appearance, viscosity, flash point, solidification point and paraffin content.

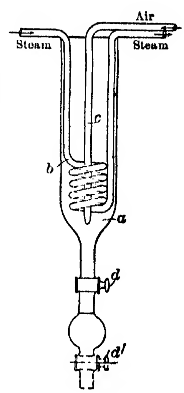


FIG. 61.

2. **For Custom House or Commercial Analysis.** Since the different laboratory distillation methods give divergent results even with the same crude oil, the style of apparatus is definitely prescribed for custom house analyses (in Germany). This is also used for the distillation of crude naphtha, kerosene, etc. The samples of oil must be treated with calcium chloride and filtered at room temperature; this separates the water present and prevents bumping.

(*a*) **Continuous Distillation** (in place of the former interrupted process) is advised,* making use of the Engler apparatus, as modified by Ubbelohde and Holde, as sketched in the Figs. 62a to 62c.

100 c.c. of oil are distilled from an Engler flask of 130 c.c. capacity. The condenser is 60 cm. long. The beginning of distillation is taken as the

* Recommended by "Der Deutsche Verband für die Materialprüfungen der Technik" and in the "Beschlüsse der Internationalen Kommission zur Vereinheitlichung der Untersuchung von Petroleumprodukten" (Wien 1912); Mitteilungen, **25**, 261 (1907).

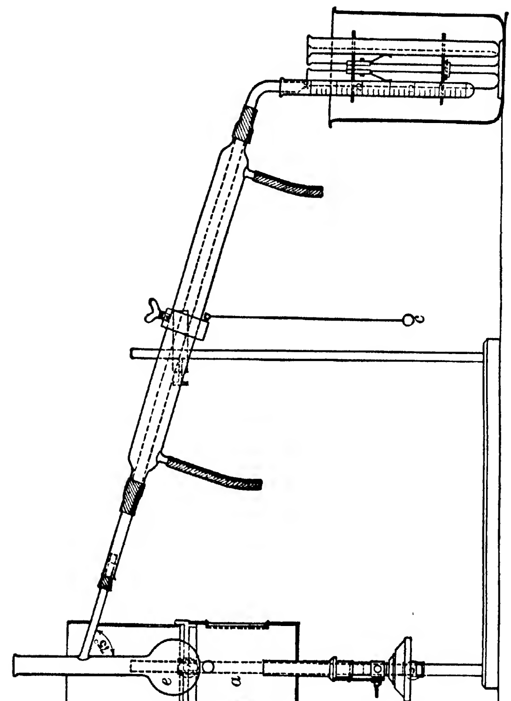


Fig. 62c.

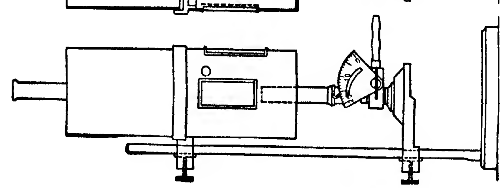


Fig. 62b.

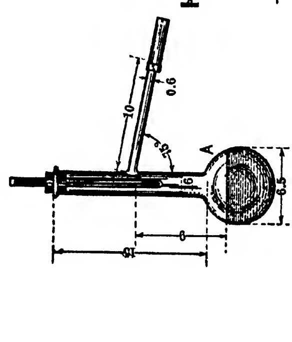


Fig. 62a.

temperature at which the first drop falls from the end of the condenser; the end of distillation is the temperature at which the bottom becomes free of liquid or white vapors appear. Two drops should fall per second; a second's pendulum allows the regulation of the speed of distillation. The distillate is caught in 6 tubes graduated to 0.2 c.c., these being held in a rotating frame and kept at room temperature by immersion in a water bath. If the individual fractions are not to be caught, it suffices to use a 100 c.c. cylinder, graduated to 0.5 c.c. in which the quantity distilled may be read at any time.

Corrections are to be made for protruding thermometer thread as given by Schlüter and Wiebe* for both the glass Engler flask and for the German official metal apparatus. For example if, in the glass apparatus, it is desired to determine the amount of distillate passing at 150°, from Table 23 it will be seen that the correction (by interpolation) for 150° is 2.5 degrees. Therefore the distillation is carried on until the observed reading of the thermometer is (150° − 2.5) or 147.5°, provided this correction for the protruding thermometer stem is to be applied.

TABLE 23

Observed boiling point	Correction in degrees Centigrade	
	With the glass Engler flask	With the official metal apparatus
60	.	0 2
80	0.8	0 5
100	1 0	0 9
120	1.5	1 4
140	2.1	1.9
160	2.8	2 6
180	3.6	3 4
200	4 6	4.3
220	5 7	5 4
240	6 9	6.6
260	8.2	8 0
280	9.7	9 3
300	11.2	10.6
320	. .	11.9

The fractions collected are generally: naphtha up to 150°, the illuminating oil fraction between 150° and 300° and lubricating oils over 300° (see page for the distillation of tar oils). In refineries using Galician or Rumanian crude oils, the limits for illuminating oils are taken 150 to 275° because they better characterize the fraction; in other

* Petrol., 7, 1304 (1912); Mitteilungen, 33, 305 (1915).

words, the origin of the oil must be considered in interpreting the results of the distillation.

Engler recommends that with lubricating oils the distillation be carried to an end in order to determine the amount of coke formed; this varies, under like conditions, according to the source of the oil and is now often determined. However, the determination of the amount of asphaltic and pitch-like materials (page 106) gives sharper comparison values.

(*b*) **For the Official German Custom-house Examination** the apparatus of Figs. 63 to 64 is prescribed;* all parts of the apparatus have fixed dimensions, and except for the flask and burette, are made of metal.

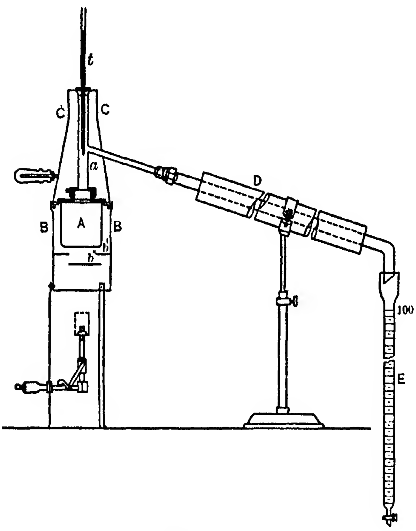


FIG. 63

FIG. 64.

100 c.c. of oil (crude naphtha, crude petroleum, etc.) are distilled from the flask *A* with an adjustable burner regulating the temperature in such a way that it rises between 120° and 150° at the rate of 4 degrees per minute and 8 to 10 per minute between 150° and 320°. At the observed temperature 320° (the zero point of the thermometer is level with the top of the cork) the distillation is stopped. The distillates are cooled by *D* and caught in the burette *E*.† The apparatus gives concordant results which are considerably different from those obtained with the same oils by method (*a*). A movement is on foot to get the permission of the German customs officials to allow the use of the glass apparatus of Engler-Ubbelohde-Holde.

In the examination of lubricating oils, distillation is continued up to 300° only. An oil is classified as a lubricating oil if nothing passes

* See Zentralblatt für das Deutsche Reich, **1898,** 279; Mitteilungen, **17,** 36 (1899).

† For details see Anleitung für die Zollabfertigung, Berlin. **1906,** Theil III, Abschn. 2, Nr. 37.

under 300° (320° measured in the oil) or if, with the oil having a specific gravity of more than 0.830, less than 70 per cent by volume passes below 300°, otherwise it is called illuminating oil. Crude oil of the properties mentioned must pay duty (Germany) as lubricating oil in case it flashes above 50° (Abel) and has a specific gravity above 0.885 at 15°, or if less than 40 volume per cent passes between 150° and 320° when fractionally distilled, or if it contains more than 8 per cent of paraffin. Naphtha, ligroin, petroleum ether should have at least 90 per cent of material boiling under 150°.

The results obtained by the methods (*a*) and (*b*) do not agree with each other, because the neck of the flask acts as a dephlegmator and the glass exerts a stronger cooling action on the vapors than the better conducting metal. This is evident from the fact that there is 20 to 35° difference in the beginning of boiling between the glass and the metal apparatus, also the quantities obtained at the beginning of distillation between the same temperature limits (as read in the vapor) are different for the two forms of apparatus, while in the neighborhood of the temperature 300° the differences disappear. These differences with the two methods are, of course, due to the fact that the temperature of the distilling vapor is read in each case, the liquids boiling in the flasks do not show these differences in temperature. Since the temperature of the boiling liquid is, as a rule, decidedly higher than that of the vapors, at the higher temperatures (over 250°), decompositions will occur in the material condensing on the neck and flowing back into the liquid.

3. Method of Bureau of Mines. This difficulty is overcome by the method of Allen and Jacobs.*

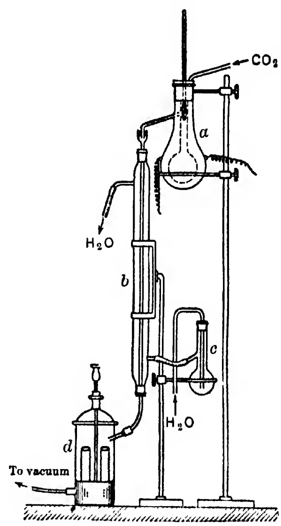


Fig. 65.

The 250 c.c. flask *a* (Fig. 65) is surrounded by a metal resistance wire for electrical heating, the neck being also wound to prevent dephlegmation, the wire being embedded in a resistant insulating material which has the general shape of the flask. The 60 cm. long Liebig condenser is placed vertically to prevent the lingering of the heavy distillates in the condenser; for the same reason the condenser water is slightly preheated if the distillates are very viscous. The rate of distillation is 1 drop per second. 200 c.c.

* U. S. Dept. of Interior, Bureau of Mines, Bulletin **19**, 28 (1912).

of crude oil are distilled in 25 degree fractions from 25° to 325°, the temperature is allowed to drop 125° (to prevent frothing when the suction is applied), the Brühl receiver attached to a water-jet pump and distillation carried on at 16 to 20 mm. mercury pressure up to 325°; if the oils contain water, the distillation is carried on in a stream of carbon dioxide (dry).

A nichrome resistance wire (0.60 Ni, 0.18 Cr, 0.22 Fe) having a resistance of 0.0046 ohms per meter at 20° is used. At the beginning a small current is used, at the end with 220 volts 3.5 amperes are applied. The difference in temperature between the bottom of the flask and the side tube is at the most 10° and decidedly less than in the case of methods (*a*) and (*b*). The insulating material is made up of 100 parts of MgO (powdered), 100 of silica, 40 of asbestos and 10 of dry sodium silicate which is rubbed to a uniform paste with a saturated solution of magnesium chloride.

The advantages of this method are: (1) the cooling of the vapors in the neck is avoided, (2) larger amounts of oil can be distilled (3) a truer conception of the actual composition of the oil is obtained than would be the case if the glass apparatus were used, (4) the upright condenser and the warming of the condenser water allow a quicker separation and a quicker determination of the boiling limits, since the distillate falls sooner into the receiver, thus allowing the reading to be taken earlier. It has the disadvantage of being more complicated and costly and the operations require a longer time. But in view of the experiments of Wiebe, it is a question if the undoubted advantages of this method would not warrant its being accepted for custom house and commercial analysis after being, perhaps, somewhat simplified.

XIII. Proximate Tests

(*a*) **Asphaltenes and Asphaltic Resins.** Varying amounts of asphaltic bodies are found in the crude oils of different countries; Russian and Pennsylvania oils contain little, Alsatian, Hanoverian and Californian oils contain considerable. A distinction is made between a hard high-melting asphaltene precipitated by benzine and a softer asphaltic resin melting below 100° and insoluble in ethyl or amyl alcohol. Both are oxygen or sulphur derivatives of hydrocarbons; as a rule, the lower their melting point, the lower will be their sulphur and oxygen content and the nearer will they approach the composition and color of the oxygen-containing parts of crude oil (see page 184).

According to Zaloziecki as well as Krämer and Böttcher the natural asphalts are obtained from the terpene-like bodies in the crude oil through polymerization and oxidation. From the work of Zaloziecki and of Engler it appears that polymerization is the main factor in the formation of asphalt while oxygen acts apparently as a catalyzer. This

view of Engler is apparently confirmed by the small amount of oxygen present in natural asphalt.

The effect of sulphur has been studied.* From olefins, mercaptans and sulphides are formed by the action of sulphur; harder and softer asphalt-like bodies were obtained as a distillation residue. Other hydrocarbons gave similar resinous and pitch-like bodies.

The formation of dark asphaltic bodies, insoluble in naphtha, soluble in benzol, by the action of air (or air under 90 to 100 atmospheres pressure) on heated light-colored oils supports the view of the formation of asphalt by oxidation of petroleum. Engler assumes that the oxidation is accompanied by a polymerization of the unsaturated hydrocarbons. The amount of asphalt in crude oils and dark lubricating oils can increase† on storage; and in diffuse sunlight the increase of asphalt insoluble in naphtha is greater than in the dark, asphalt itself being sensitive to light.

The asphalt bodies precipitated by ether-alcohol (3:4) in amounts up to 15 per cent from Wietze crude oil contain considerable sulphur, as do also many other asphalts.‡ In an asphalt obtained by precipitation with naphtha from a dark railroad oil (probably of German origin) was found two per cent of sulphur.

The following precipitation methods are used in the determination of the amount of asphaltenes and softer resins in an oil; since, depending on the nature of the solvent and the precipitant, different asphaltic bodies are obtained, the precipitated bodies do not represent absolute, but only comparative values. If the precipitation is to be made with naphtha, only the lowest boiling fractions (free from aromatic hydrocarbons) should be used, for the solubility of asphaltenes is less the lower the boiling point of the naphtha while on the other hand they are soluble in aromatic hydrocarbons. An Alsatian oil with 40 volumes of naphtha (boiling limits 60 to 80°) gave 2.1 per cent, while with a naphtha boiling below 50° the amount of asphalt precipitated was 5.5 per cent; with a naphtha boiling under 41°, the amount of asphalt was 5.7 per cent. For comparative results the same naphtha must be used and in the quantitative determination of naphtha-insoluble asphalt a " normal benzine " is recommended (see page 127).

1. Qualitative Detection of Asphaltenes and Asphaltic Resins. 1 c.c. of oil is shaken with 40 c.c. of " normal benzine " (naphtha) in a test tube and allowed to stand over night. In dark colored oils the insoluble asphaltenes separate in dark

* Friedmann, Petroleum, **11**, 693, 978 (1916).

† Holde, Mitteilungen, **27**, 146 (1909); Meyerheim Chem. Ztg., **34**, 454 (1910).

‡ Kayser, Untersuchung über die natürlichen Asphalte, Nürnberg, **1879**.

flakes which on collection on a filter paper resemble asphalt; these flakes are dissolved in benzol, the solvent is evaporated and a material not melting on the water bath obtained.

If 0.5 c.c. of oil is dissolved in 14 c.c. of ethyl ether and then 7 c.c. of 96 per cent alcohol added, the harder asphaltenes insoluble in naphtha precipitate together with softer pitch-like bodies, forming a tough mass which clings tenaciously in clumps to the side of the vessel. It is soluble in benzol and melts on the water bath.

2. Quantitative Determination.

(α) **Asphaltenes Insoluble in Naphtha.** 5 grams of oil are shaken in a 500 c.c. bottle with 40 times its volume (220 c.c. assuming the sp. gr. to be 0.9) of "normal benzine." If the oil contains only little asphalt, as much as 20 grams of oil may be taken with the corresponding amount of naphtha. After standing at least 24 hours at a temperature between 15° and 20° and away from direct sunlight, the solution is decanted through two filters folded together (white ribbon, S & S). The residue is washed with naphtha till the filtrate gives no more oily residue. To prevent the asphalt from becoming insoluble on standing, it is at once dissolved in hot benzol, the main mass evaporated from a flask and the remainder in a tared vessel, the residue dried at 105° and weighed. Foreign substances precipitated by naphtha and insoluble in benzol can be separately determined by using a weighed filter paper. If the suspended asphalt is to be determined, the amount of asphalt is determined in the original oil as well as in the filtered oil; the difference gives the suspended asphalt.

Ubbelohde and Allen* have found that with cylinder oils paraffin-like bodies are precipitated with the asphalt; these are separated (as in β) by extraction with boiling alcohol.

Bodies precipitated by the "benzine" but insoluble in benzol are separately determined.

(β) **Asphalt Insoluble in Alcohol-Ether (1 : 2).** 5 grams of well-mixed oil in a 300 c.c. glass-stoppered bottle are dissolved in 25 volumes of ethyl ether of specific gravity 0.72 (137.5 c.c., sp. gr. of oil assumed 0.9) at room temperature. With constant shaking 12.5 volumes of 96 per cent alcohol (68.5 c.c.) are added slowly from a burette. After a final shaking, it is allowed to stand 5 hours at 15°, then filtered rapidly through a pleated filter (white ribbon, S. & S. 589). The bottle and filter are then washed with a mixture of (96 per cent) alcohol and ether (1 : 2) until about 20 c.c. of the filtrate evaporated give only traces of tarry matter. The washed asphaltic pitch, which still contains paraffin and soft resins, is dissolved from the sides of the bottle and from the filter paper by means of hot benzol and evaporated in a tared glass dish containing a weighed glass stirring rod. According to a suggestion of Engler and Albrecht† the residue is boiled with 30 c.c. portions of absolute alcohol, rubbing with the glass rod, until the extracts on cooling and shaking give no precipitate of paraffin; it is then dried at 105° and weighed.

The method of leaching with alcohol is used when the residue of pitch and paraffin is not too great (a few tenths of a per cent) or has only a light brown but not black color. If, however, a considerable amount of asphalt has been obtained, the

* Chem. Umsch., **20,** 192 (1913).

† Ztsch. für. angew. Chem., **14,** 913 (1901).

method is uncertain, since it is difficult to tell when all the paraffin has been extracted. For this reason the device of Holde and Meyerheim* was suggested. The extraction apparatus is shown in Fig. 66; it avoids the use of cork. At the bottom of the condenser are two glass hooks on which the extraction thimble is hung with nickel wire or with twine. The method of use is the following. The mixture of pitch and paraffin is precipitated as above, washed, dissolved in benzol, the solvent evaporated, the residue weighed after drying at 105°. The residue is dissolved or suspended in 10 c.c. of ether, 2 grams of bone-black previously extracted with alcohol are added together with 10 to 15 grams of rough sand, the ether evaporated carefully on a water bath, the entire mass put into the extraction thimble, the latter being closed at the top with a wad of cotton to better distribute the solvent. The last traces of paraffin and asphalt in the dish are removed (to the thimble) by solution in a little ether, addition of sand and bone-black and treatment in the same manner as in the case of the main portion. The thimble is hung on the condenser and extracted with absolute alcohol until by a final extraction of one hour not more than 1.5 milligrams are obtained. The collected alcoholic extracts are evaporated and the residue weighed; the asphalt is the difference between the first (pitch plus paraffin) and the second (paraffin) weighings.

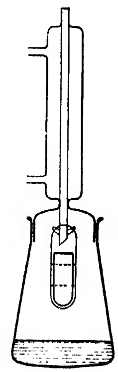


FIG. 66.

In order to facilitate the settling and extraction of the precipitated asphaltenes and resins, the following modification† was suggested:

The oil is treated with ether-alcohol (2 : 1) as usual, then several drops of ethereal ferric chloride and then a few cubic centimeters of alcoholic ammonia are added. The precipitate formed drags down with it the suspension of asphaltenes and resins; the precipitate can then be readily filtered and extracted with benzol.

The procedures (α) and (β), especially the first, are of technical importance and accepted in the industry; method (α) is used in the examination of cylinder oils and railway axle oils, method (β) which, however, is more tedious and slower, is used for cylinder oils. Since in recent years the oils used by the Baden State Railways and by large industrial plants have been examined for soft pitch-like bodies, the complaints about formation of carbonaceous and similar residues in the cylinders, etc., have decidedly decreased. The method described under δ has not yet been sufficiently tested and is not much used.

(γ) **Asphalt Insoluble in Amyl Alcohol.** According to Dæschner,‡ amyl alcohol will precipitate asphaltenes and softer resins from residues containing them; for example, 18 per cent of asphaltic material can be obtained from the Wietze oil. One of the difficulties of this process, is the relative insolubility of cylinder oils in amyl alcohol.

* Chem. Ztg., **35**, 369 (1911).

† Chemiker Zeitung, **37**, 1145 (1913).

‡ D. R. P. 124980

(δ) **Asphalt Insoluble in Ethyl Acetate** is obtained according to Koettnetz* by treating crude oil with an equal or double weight of ethyl acetate; it is precipitated easily, avoiding decomposition during the purification of the oils. The method has not yet been used in analysis.

Koettnetz and Kantorowicz recommend the following procedure:

2 to 5 grams of oil with twenty times as much fresh ethyl acetate are boiled for twenty minutes under a reflux condenser, poured through a pleated filter, the residue washed with the ester till the filtrate contains no oil or paraffin. The asphalt on the filter is dissolved in benzol and, after evaporation of the benzol, is determined in the usual manner. Ethyl acetate recovered by distillation must not be used.

Holde and Meyerheim have found that ethyl acetate precipitates more asphaltenes than does "normal benzine" but less than benzine boiling at 50°.

(*b*) **Paraffin.** 1. The following method† is used by the German custom house authorities.

100 grams of crude oil are distilled rapidly from a tubulated retort till the temperature of 300° is reached. A weighed receiver is then put into position (without a condenser) and all oil driven over until the residue cokes completely (without thermometer); the amount of heavy oil distilled is determined.

The heavy oil distillate thus obtained is analyzed for paraffin as follows, the amount of paraffin in the original oil being calculated from the amount in the distillate. The amount of paraffin in light oils is determined directly without distillation.

5 to 10 grams of the substance are dissolved at room temperature in a mixture of ether and absolute alcohol (1 : 1) to a clear solution, then cooling to − 20°, just enough alcohol-ether mixture added till all oily drops are dissolved and only paraffin flakes are visible. With much paraffin, it is advisable to warm with ether to complete solution and then add the same volume of alcohol. The precipitated paraffin is then filtered on a funnel‡ surrounded with a rocksalt and ice freezing mixture (Fig. 67), all traces of the alcohol-ether solution, being removed, and then washed free from oil by means of cooled alcohol-ether. The filtrate is evaporated and the

* D. R. P. 191839.

† This depends on the precipitability of paraffin by alcohol in ether solution: Petrol., **4,** 873 (1909); Ding. Poly. Jour., **262,** 473 (1886); Chem. Ztg., **17,** 1473 (1893); Mitteilungen **14,** 211 (1896). The final form is due to Holde. For other methods see Ber., **21,** 2973 (1888); Chem. Ztg., **17,** 1473 (1893); Ding. Poly. Jour., **267,** 274 (1888); these are only applicable to particular materials and are not general.

‡ A very useful arrangement for filtering cold has been constructed for Eisenstein and Ziffer (Chem. Ztg., **33,** 1330 (1909) by the Vereinigten Fabriken für Laboratoriumsbedarf, Berlin.

process of precipitation repeated. The combined residues are then washed into a weighed glass dish with hot benzol or naphtha and the solvent evaporated on a water bath. The paraffin is carefully washed with cooled alcohol-ether until 5 c.c. of the filtrate on evaporation will give no residue, or only a trace of material solid at room temperatures, is obtained; too prolonged washing is to be avoided because of the still quite noticeable solubility of paraffin in alcohol-ether. If on cooling, the paraffin is seen to be hard, it is heated at 105° for 15 minutes and weighed after drying in a desiccator; if the paraffin is soft (with melting point under 45°), it should be dried several hours in a vacuum desiccator at 50° before weighing.

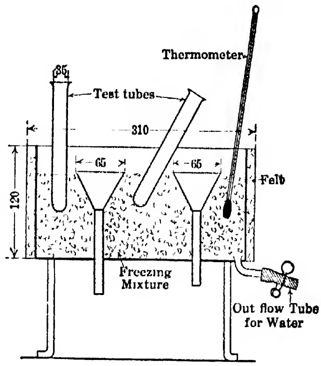


FIG. 67.

The paraffin is at times brown in color because of resins precipitated with it. It is then several times treated with boiling alcohol and decanted hot, the resinous bodies remaining insoluble. If this is not sufficient, it must be purified with several per cent of sulphuric acid or filtered through fuller's earth or bone-black while dissolved in naphtha.

In the analysis of solid paraffin masses 0.5 to 1.0 gram is dissolved in 10 to 20 c.c. of alcohol-ether (see also page 249).

A correction must be applied: 0.2 per cent is added in the case of completely liquid distillates, because of slight solubility in alcohol-ether; if the substance solidifies at +15°, 0.4 per cent is added; if the sample is solid, 1 per cent is added. This method determines the amount of paraffin in a distillate available for candle manufacture. Softer paraffins melting under 50° are not completely precipitated, being quite soluble in alcohol-ether. They may, however, be determined by evaporating the filtrate and dissolving in a little alcohol-ether (2 : 1) and precipitating by cooling to −20° or a still lower temperature. In the distillation of crude oil (which is necessary as above described only in the case of dark oils) a small amount may be decomposed (with a content of 5 per cent, this may be as much as 0.5 per cent) and will not be found in the distillate. This error is the more noticeable the higher the content of paraffin in the crude oil.

When the total amount of paraffin is to be determined, it is not possible to distill* at so high a temperature, for, as has already been stated, paraffins are decomposed in that operation. The following method is suggested:

The oil is distilled to only 250° to separate the lighter portions, the residue is washed with light benzine into a separatory funnel, and then shaken with a mixture of equal parts of concentrated (1.84) and fuming sulphuric acid. After 36 hours the acid layer is separated, the oil washed with alkali and then with hot water and then the benzine is evaporated. In the light-colored residue the paraffin is determined as above.

* Scheller, Petroleum, 8, 905 (1913).

2. It is said that by using butanone* (methyl-ethyl ketone) it is possible to precipitate even soft paraffins with one operation; the alcohol-ether precipitation requires two treatments. It is claimed that the temperature need not be so definitely low.

1 to 5 grams of distillate are dissolved at room temperature in the least amount of butanone (to which has been added 1.3 per cent of water to give a density of 0.812 at 20°). The mixture is cooled to $-20°$, enough solvent being added to keep the oil in solution. The precipitate is collected on a cold funnel (Fig. 67) and washed with (0.812) butanone till free from oil; this takes 5 washings with 10 c.c. of butanone. The paraffin (after removing the funnel from the freezing mixture) is dissolved in benzine or benzol, the solvent then evaporated and the paraffin residue weighed. See page 249.

(*c*) **Formolite Reaction (Nastjukoff Test).**† When formaldehyde in the presence of concentrated sulphuric acid is added to a mineral oil the unsaturated cyclic hydrocarbons are precipitated; in this way a yellow solid is obtained for which the name "formolite" has been suggested. The formolite number is the number of grams of dried formolite which are obtained from 100 c.c. of oil under definite conditions.

The different classes of hydrocarbons occurring in petroleum react with sulphuric acid and formaldehyde as follows:‡ paraffin hydrocarbons and saturated naphthenes are not attacked; olefins give a red-brown syrupy liquid; unsaturated naphthenes give a red-brown precipitate easily soluble in water; aromatic hydrocarbons give a bright red or green precipitate insoluble in water.

Nastjukoff found that American oils gave a higher formolite value than did Russian oils. Heer advises the testing of crude oils directly instead of after treatment with sulphuric acid as was proposed by Nastjukoff.

Nastjukoff has found the formolite values of various American and Russian oils, the results indicating that all these oils consist mainly of unsaturated cyclic hydrocarbons; American cylinder oil gave the value 92 to 97, Russian cylinder oils 58 to 87, vaseline oils 7.8 and 22. The formolite value ought to give valuable information regarding crude naphtha.

Heer§ found that the use of methylal $CH_2\begin{matrix}\diagup OCH_3\\ \diagdown OCH_3\end{matrix}$ instead of formal-

* Schwarz and Huber, Chem. Umschau, **20,** 242 (1913).

† Petrol., **4,** 1336, 1397 (1909).

‡ Severin, Petrol., **6,** 2245 (1911).

§ Chem. Ztg., **34,** 893 (1910).

dehyde was advantageous, because it acts both as a solvent and as a condensing agent and, furthermore, as his experiments with artificial mixtures of naphtha and small amounts of benzol show, it is a better reagent for the detection of benzol hydrocarbons than is formaldehyde. Marcusson* in his work on the composition of mineral oils recommended the following method:

27 grams of oil are dissolved in 50 c.c. of "normal benzine" in a 300 c.c. Erlenmeyer flask and 30 c.c. of conc. sulphuric acid added without shaking. To the mixture cooled with ice water, 15 c.c. of 40 per cent formalin are added and the flask shaken in the cooling mixture until no more heat is evolved. The reaction mixture is allowed to stand for half an hour at room temperature and then transferred to a liter flask containing 200 c c of ice water, rinsing with water. The acid is then neutralized with ammonium hydroxide in excess and the resulting precipitate caught on a filter (Buchner funnel). It is washed first with naphtha to remove oil, then with water to remove NH_4OH and then dried at 105° to constant weight. From the naphtha solution (which has been separated from the aqueous in a separatory funnel) after distilling the solvent, that part of the oil not reacting with formalin and sulphuric acid is obtained.

The properties of the unsaturated cyclic hydrocarbons are determined through a comparison of the original oil with that portion obtained on evaporating the naphtha solution. Those portions recovered are always specificially lighter and have a lower refractive index than the original. Those substances giving the formolite reaction must, therefore, have a higher specific gravity and a higher refractive index than the original oil. Moreover, the viscosity of the recovered oil is higher than the original; it follows that the formolite portion does not give the lubricating power to an oil.

(*d*) **Sulphur Dioxide Method.** In this procedure† the petroleum distillate is shaken with liquid sulphur dioxide at a low temperature; aromatic and cyclic unsaturated hydrocarbons dissolve, paraffins and naphthenes remain undissolved. Under proper conditions, a separation is possible.

Apparatus: A thick-walled graduated burette (*A*) of 200 c.c. capacity (Fig. 68); a cylindrical container (*B*) of 230 c.c. capacity (Fig. 69); two cooling baths for the vessels (*A*) and (*B*), consisting of two concentric tinned cylinders, the outer vessel containing a freezing mixture, the inner a cold-conducting material (a kerosene distillate) (Figs. 68 and 69); a flask with graduated neck; a wash bottle for liquid sulphur dioxide (a Dewar flask).

Into the graduated burette (*A*) is put 50 c.c. of the distillate to be examined, while into the container (*B*) is run twice as much liquid SO_2 by weight; both vessels are then cooled to − 12°. The vessel (*B*) is filled as indicated in Figure 69. Liquid

* Chemiker Zeitung, **35,** 729 (1911).

† Edeleanu, Petroleum, **9,** 862 (1914).

SO_2 is run from *B* to *A* until after shaking two layers remain; then one-third of the remaining SO_2 is run in. After recooling to $-12°$ and shaking, the lower layer is run into a Dewar flask; then again SO_2 is added to *A*, cooled, shaken and separated, catching all the separate SO_2 extracts in the same Dewar flask. The undissolved saturated hydrocarbons remain in the burette (*A*).

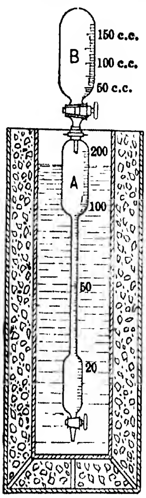


Fig. 68.

With high-boiling distillates, as gas oil or lubricating oil, it is sufficient to simply evaporate the SO_2 and estimate the proportion of hydrocarbon groups either by direct weighing or from the specific gravities and volumes of the materials. With low boiling distillates (naphtha and kerosene) the evaporating SO_2 will carry with it considerable amounts of hydrocarbons. The SO_2 is therefore not evaporated, but is absorbed in alkali as follows: After running off the SO_2 layer the burette (*A*) is attached to the flask (in Fig. 70) and the oil run into the alkali through a narrow tube; the SO_2 is thus neutralized. After cooling the flask and contents, water is run in at the side until the oil rises to the graduated portion of the neck of the flask. The volume can thus be read, the specific gravity is then determined, and thus the amount of saturated hydrocarbons; the unsaturated hydrocarbons are estimated by difference.

By this method it is possible to get results which check. The separation causes no change in composition (as do nitric and sulphuric acids). Aliphatic unsaturated hydrocarbons are said to cause difficulties. The method allows a physical separation of components and thus gives valuable data for certain industrial operations.

(*e*) Engler suggested the separation of saturated and unsaturated hydrocarbons by shaking with concentrated aqueous mercuric acetate

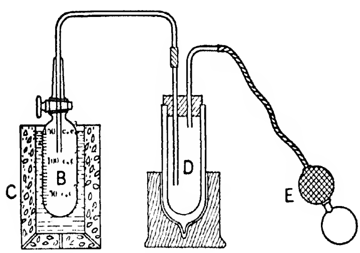


Fig. 69.

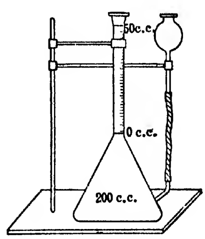


Fig. 70.

solution in which olefins and cyclic unsaturated bodies are soluble in the cold; on heating, the hydrocarbons are oxidized, mercurous acetate forms and precipitates. Butylene is colored red, amylene yellow, and hexylene takes on a rose color.

In making a quantitative determination the major portion of unsaturated compounds is extracted by shaking with aqueous mercuric acetate and reprecipitated with hydrochloric acid; the rest of the unsaturated compounds are destroyed by boiling with fresh mercuric acetate under a reflux condenser. The stable hydrocarbons are then distilled off, and their amount determined. The unsaturated hydrocarbons are estimated by difference.

(*f*) **Sulphur.** For qualitative and quantitative tests see page 77. It may be determined by the method of Engler and Heussler (page 140), the crude oil being burnt in the lamp with a suitable sulphur-free solvent. The best solvent* is a mixture of 5 parts of ether, 45 parts abs. alcohol, 20 parts of amyl acetate and 20 parts of refined illuminating oil (treated with sodium) to which 5 to 10 per cent of crude oil has been added (the more viscous the oil, the less the amount added). For a light oil free from asphalt, desulphurized kerosene is enough. Table 24 gives the sulphur content† of some petroleums.

TABLE 24

Origin	Sulphur per cent	Origin	Sulphur per cent
Alsace	0 34 to 0 67	Texas	1 7 to 2 6
Pechelbronn	0 13 to 0 14	Alaska	0 10 to 0 12
Hanover	0 08 to 0 09	Canada	0 92 to 0.99
Pennsylvania	0 03 to 0 55	Baku	0 07 to 0.29
Ohio	0.5 to 1 0	Italy	0 59 to 4.71
California	0.06 to 1 0	Japan	to 0.83

XIV. Physiological Properties

The physiological properties‡ of crude oil and similar materials (lignite tar, shale oil, etc.), since they are mixtures of many components or groups of substances such as naphtha, kerosene, paraffin, lubricating oil, are the result of the combined action of the single parts of the mixture.

Several of the high boiling petroleum products are used with success in medicine (dermatology), notably vaseline, "paraffinum liquidum" and "naphthalan," as the basis for salves. The ill effects of

* Albrecht and Spanier, Dissertations, Karlsruhe, **1907** and **1910**.

† Engler-Höfer, I, 468.

‡ Lehrbuch der Toxicologie, Lewin, **1897**, II Auflage, 202; Th. Weyl, Die Krankheiten der Petroleum Arbeiter, Handbuch der Arbeiter-Krankheiten, **1907**, 210; A. Hoffmann, Die Krankheiten der Arbeiter in Teer und Paraffin Fabriken. Vierteljahrsschrift für gerichtliche Sanitäts-wesen, III F., 5 Bd., Heft. 2 und 6; W. Ebstein-Göttingen in Engler-Höfer, Bd. I, **1913**, 774.

other products have been demonstrated. Probably the more harmful action of the higher boiling fractions, such as crude paraffin, is due to the insufficient treatment of the crude materials for the removal of oxygen and sulphur derivatives; on removal of harmful components certain mineral oils seem to possess a decided ability to excite connective tissue due probably to a content of unsaturated terpene-like bodies; they are used for the cleansing of wounds and as an aid to the healing process.

Workers in the petroleum industry are liable to poisoning from various products and are subject to skin diseases. Crude oil in the form of vapor or as liquid may cause poisoning of the skin. Workmen exposed to naphtha fumes become unconscious and are liable to be asphyxiated; the pupils become small, the pulse hardly noticeable, coughing and choking result and, as a secondary action, inflammation of the lungs occurs, and if the naphtha is frequently inhaled, death may result. Pure naphtha vapors cause unconsciousness, disturbance of breathing, vomiting, etc., and it seems, according to the accounts in the literature, that pentane is the harmful substance. Introduced in the liquid form 12 grams of naphtha or 750 grams of kerosene will cause death; the kerosene however does not appear in the urine. High boiling oils when administered cause pains in the stomach, vomiting, etc. According to H. Wolff* naphtha vapors are poisonous to mice and benzol vapors cause death. The skin is more irritated by benzol derivatives than by naphtha, the former causing the formation of blisters, peeling of the skin, and in some cases formation of pus

The first observation of skin disease caused by petroleum products was made by Lewin in Pennsylvania. At the pumps the workmen are affected with acne and with mattery pimples, boils, etc. Skin diseases found among workers in printing establishments† are probably due to the poisonous action of benzine and benzol. The use of pure turpentine oil or refined petroleum products for the cleansing of plates and type has rarely caused trouble but the use of benzol-containing turpentine substitutes has produced reddening, tension and blisters of the skin, as in burning; later stages have shown a typical artificial eczema.

With those workmen who press out the oil from crude paraffin, a "petroleum itch" may result, generally on the back of the hand. Paraffin is said to cause carcinoma. The petroleum itch is said to be due to the improper functioning of the sweat glands of the skin. According to Hoffman (supported by several reports from practice) it is

* Karbid u. Azetylen, **1911,** 273.

† Zellner and Wolff, Zeitschr. f. Hygiene u. dufekt. Krankh., **75,** 69 (1913).

possible that lignite-tar oils irritate the skin and also cause the so-called paraffin itch. Irritation of eyes and nose can be caused by insufficiently purified brown-coal tar products which contain creosote-like bodies. Many laborers, employed in an asphalt plant developed after a time an acne-like disease of the whole body.

B. Naphtha

I. Definition

"Benzine" or "naphtha" is usually that portion of crude oil distilling up to 150° C., but this limit is not always observed; under the term naphtha are sometimes included oils with high flash point (over 21°) and boiling up to 230°, which cannot be used as illuminating oil in an ordinary Kosmos burner with the ordinary chimney, but are used as turpentine substitutes and as solvents in varnish making. (See page 128.) The crude naphtha generally contains portions of higher boiling fractions which are separated on redistillation and either added to the illuminating oil fraction or used as a turpentine substitute. According to the method of treatment used in practice, the boiling limits will vary, so that nothing definite can be said on this point.

Naphthas distilled in the usual manner have very small iodine values as they contain saturated hydrocarbons which do not absorb iodine. Gasoline obtained by the Burton process* from heavier oils may have an iodine value as high as 139.

The specifications for naphtha differ according to the use to which it is to be put. Usually a certain specific gravity is demanded, or boiling limits are stated; material with the least odor and slightest color is considered most desirable.

Petroleum ether (specific gravity 0.65 to 0.67) is used for solvent purposes, sometimes for lighting, also as a lubricant for liquid air machines as it freezes† below −160° C.

Gasoline is used to a small extent for producing gasoline gas (gasoline vapor and air), and to an enormous degree as a motor fuel. The German Automobile Club specifies for pleasure cars a gasoline of specific gravity 0.685 to 0.700, recommending for commercial cars 0.705 to 0.720.

In general, gasolines of high specific gravity are not used for passenger cars, because they cause irregular ignition, fouling and corrosion.

* Kissling, Petroleum, **11**, 753 (1916).

† Formanek, Knop and Korber, Chemiker Zeitung, **41**, 713, 730 (1917); also **41**, 789 (1917).

In England motor-buses have been run on a petrol with density as high as 0.76 but high-boiling fractions were absent. The specific gravity cannot alone be taken as the measure of the value of the motor spirit. Since it is the fraction boiling over 150° which causes the fouling of the cylinders, it follows that gasolines of specific gravity under 0.720 and over 0.700 which are free from such components will be more satisfactory than a gasoline with lower gravity, but containing considerable quantities of high boiling components. Thus a sample of American naphtha of specific gravity 0.68 when mixed with a Russian naphtha of specific gravity 0.74 gave a blend of density 0.70 but since it contained a large amount of material boiling above 100° C., it was not usable.* Tests for examination of other motor fuels (benzol, alcohol, acetone, ether, etc.) have been described.†

The ordinary commercial naphthas should be as free as possible from components boiling over 100°; if used for cleaning, they should have a minimum of unpleasant odor, since this is difficult to remove from the fabrics. For the extraction of oil from seeds and meal, a product boiling near 100° should be used, so that the material will be already at that temperature when extraction is begun; otherwise water might condense and cause the extracted mass to become pasty.‡

It has been suggested that instead of using the arbitrary terms, rigolene, petroleum ether, gasoline, ligroin, etc., it would be more definite to describe certain fractions as naphtha of certain boiling limits (for example, 65/95); such a procedure would give the consumer a better means of judging his material than is given by the specific gravity. It has also been suggested that a naphtha be described by stating what per cent will distill under 100°; thus a 90-naphtha would mean that 90 per cent distilled under 100° C. Such a method is used in describing benzols.

II. Specific Gravity

For the significance and determination, see page 1. In the determination of the specific gravity, the values may be recalculated to the normal temperature (15°) by the correction table due to D. Mendelejeff.

* Zeitschrift fur angewandte Chemie, **21**, 371 (1908).

† K. Dieterich, Unterscheidung und Prufung der leichten Motorbetreibsstoffe. Berlin, 1916. Verlag des Mittel-europischen Motorwagenvereins.

‡ Ubbelohde, Handbuch, Bd. 1, 606.

TABLE 25

For a specific gravity of	Correction for one degree difference in temperature	
	Russian oils	Pennsylvania oils
0.700 to 0.720	0.00082	0.00086
0.720 to 0.740	0.00081	0.00082
0.740 to 0.760	0.00080	0.00077
0.760 to 0.780	0.00079	0.00072
0.780 to 0.800	0.00078	0.00068

III. Volatility

Extraction benzine or motor spirit should leave no residue on evaporation on a watch-glass. On filter paper, it should not leave an oily residue; such a residue would indicate high boiling fractions. Dieterich suggests that by placing 10 c.c. of sample on a watch-glass and weighing after 10 minute intervals of exposure to the air at ordinary temperature a light gasoline will evaporate in 2 hours, medium gasoline requires 2.5 hours and heavy naphtha needs 4 hours; motor benzol requires 3.5 hours.

IV. Fractional Distillation

In the case of internal combustion motors, the petrol is evaporated in a special chamber before entry into the explosion cylinder. For judging the uniformity and rapidity of evaporation the distillation test is very important; this test is also valuable in judging the worth of a solvent naphtha.

(*a*) **The Ordinary Commercial Test.** 100 c.c. of naphtha are distilled directly from the Engler flask as described on page 99 and ten-degree fractions caught. If the barometric height is not normal, the difference must be taken into consideration.* The distillates are not to be read at the even 10° mark but at a figure as much higher or lower as the boiling point of water is higher or lower than 100° under the same conditions; that this correction is adequate for industrial purposes has been shown by Kissling. The corrections are to be considered if the barometric pressure varies more than 5^{mm} from the normal. A simple apparatus, which allows distillation at 760^{mm} by using a small water

* Ubbelohde, Ztsch., für. angew. Chem., **19**, 1155 (1906); Kissling, **32**, 695 (1908).

column, has been described by Bunte* and found very useful by Scheller. The lowering of the boiling temperature for naphtha and kerosene is 0.035° per one millimeter decrease in the atmospheric pressure.† Thermometer correction, see page 101.

(*b*) **For Custom-house Examination.** The examination is to be made as described on page 102. The classification of materials is described on the same page.

V. Vapor Pressure

The vapor pressure must be considered in storing naphtha and similar inflammable liquids. To determine the vapor pressure a Torricellian vacuum is prepared according to Kohlrausch (Praktische Physik) in a tube of 1 meter length and 10 mm. diameter. The air is expelled from the mercury by boiling, the tube then inverted in a trough of mercury. The height of the column is then read from a scale attached or by means of a cathetometer. An excess of substance is then introduced by means of a curved pipette; the liquid, on rising to the top evaporates quickly, and in some cases violently (to avoid cracking tube, incline it while introducing liquid). An excess of liquid must be present to establish equilibrium. The column of mercury is depressed and the height is again read; the difference between this value and the original gives the vapor pressure of the substance. By surrounding the tube with a jacket, the determination may be made at the temperature of steam or at the boiling points of other liquids. (Fig. 71.) A correction must be made for the pressure exerted downward by the small layer of excess liquid on the surface of the mercury. If s is the specific gravity, h is its height, then $\frac{(h)\ (s)}{13.6}$ must be subtracted from the difference in height of the two columns of mercury. At higher temperatures a correction must be made for the vapor pressure of mercury.‡

VI. Flash Point

This is sometimes asked for to estimate its inflammability in the motor. The flash point is useful also in estimating the fire risk. Petroleum naphtha generally flashes below 0°; the flash point being taken in an Abel tester (Fig. 72).

The naphtha is put in the vessel *a* of the Abel tester (for a description see page 135). It is cooled by a mixture of solid carbon dioxide and alcohol placed around it

* Liebigs Annalen **168**, 139 (1873); Chemiker Zeitung, **38**, 917 (1913).

† Chemiker Zeitung, **37**, 897 (1914).

‡ See Landolt-Börnstein, Tabellen.

in the tinned vessel *b* which in turn is surrounded by the enameled lead jar which also contains some of the freezing mixture and which is insulated with felt. The temperature will drop to − 60°; the entire apparatus is wrapped in towels or packed in sawdust to prevent warming. The ignition apparatus is put into the cover of *a* shortly before testing to prevent freezing of the oil in the wick of the test flame and to prevent its extinguishment during the experiment. The mechanism which serves to dip the test flame into the vessel works poorly at the low temperature and must be frequently helped by turning the winding-up screw at the top. A test is made every one-half degree as with illuminating oil; to do this the vessel is taken out of

FIG. 71.

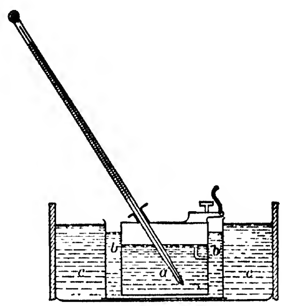


FIG. 72.

the freezing bath and wrapped in a towel, in this way avoiding the possibility of the constantly escaping carbon dioxide extinguishing the pilot. The testing is begun at − 50° to − 60°. A correction for the height of the barometer or for the protruding stem of the alcohol thermometer is not applied.

To determine the burning point the cover of the tester is removed, the thermometer fastened to a stand and, at every half degree, a flame from an ordinary blowpipe is led over the surface of the naphtha. The burning point is the temperature at which a constant burning on the surface of the naphtha results.

The flash and burning points of several naphthas are here given:*

Boiling limits of the sample	50/60°	60/78°	70/88°	80/100°	80/115°	100/150°
Flash point under .	− 58°	− 39°	− 45°	− 22°	− 21°	+ 10°
Burning point . . .		− 34°	− 42°		− 19°	+ 16°

The difference between the flash and burning points of naphtha is not large, and is very much smaller than the difference of these values for

* Mitteilungen, **17**, 70 (1899).

lubricating oils. For comparison, the flash point of absolute alcohol is + 12° at 768 mm., for 94 per cent by weight alcohol + 18°, 70 per cent alcohol 22°, 50 per cent 26.5°, for benzol it is − 8° (700 to 713 mm.), for turpentine between 30° and 32°, and for turpentine substitute it is over + 21° C. (see page 42).

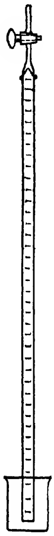


FIG. 73.

VII. DANGER OF EXPLOSION

The difference between inflammable and explosive should be emphasized in this connection. In internal combustion motors, the attempt is made to get an explosive mixture of naphtha and air which on extremely rapid combustion (explosion) develops power. However, only certain mixtures of inflammable gases with air are explosive. If an excess of either air or gas is present, an explosion will not take place; since with a given amount of gas reacting, much excess material is to be heated, the temperature of the gas mixture will not increase as much as when no non-reacting substances are present, and, consequently, the velocity of reaction will not increase enough to cause the very rapid reaction known as an explosion. The explosive limits of certain gas mixtures have been determined by Bunte,* using a gas-burette 19 mm. in diameter in which the gas mixture was confined over water and ignited by an electric spark. (Fig. 73.)

TABLE 26

Kind of gas	Per cent inflammable gas in mixture		
	No explosion	Explosion	No explosion
1. Water gas	12.3	12.5 to 66.6	66.9
2. Illuminating gas	7 8	8 0 to 19 0	19.2
3. Benzol vapor	2.6	2.7 to 6.3	6.7
4. Pentane	2.3	2.5 to 4.8	5.0
5. Naphtha	2.3	2.5 to 4.8	5.0

To insure uniformity, these experiments were performed under the same conditions, since the explosive limits not only depend on the kind of gas but also on the width of vessel used, the method of ignition, the pressure and the temperature. The limits for naphtha are small; since, however, traces of naphtha are enough (difference from water gas

* Jour. f. Gasbel., **44**, 835 (1901).

and illuminating gas) to form an explosive mixture, the danger is correspondingly greater. Liquid alcohol can be ignited with a naked flame or an electric spark, but not certainly with glowing charcoal. Alcohol vapor explodes with air when 5.2 per cent is present in air.*

The following method can be used for testing the explosiveness of naphtha-air mixtures: A definite amount of low-boiling benzine, the volume of which can be calculated, is evaporated into a gasometer which also contains a definite amount of air over water. Some of this mixture is sucked into a Hempel explosion pipette previously filled with mercury and exploded by an electric spark.

Table 27 shows the relation† between the explosion limits, the velocity of ignition and the vapor pressure.

TABLE 27

	Velocity of ignition cm/sec	Boiling point	Vapor pressure at 20° C. mm. Hg.	Explosion Limits
Pentane.	57	35 to 40	424	2 4 to 4.9
Hexane. . .	54	65 to 70	124	
Benzol....	32	80 to 85	75	2 65 to 6.5
Gasoline . .	68	30 to 85	. .	.
Benzine....	31	90 to 110	.	2.1 to 4.9

The velocity of ignition‡ is the speed at which the visible inner cone of the Bunsen flame travels back against the on-coming mixture of gas and air; with a quiet Bunsen flame, the inner cone is in a state of dynamic equilibrium. The ignition velocity is obtained by dividing the velocity of efflux by the surface of the inner cone.

With heating appliances, the mixture of naphtha and air must be kept above the upper limit, while with motors the lower limit of explosiveness is desired, since the object is to get as much power as possible with a given amount of gas. The more violent explosions obtained with richer gas mixtures are not so completely absorbed by the movable parts of the motor as the slower, more deliberate expansions of the gas mixtures low in naphtha.

* Jahrbuch der Spiritus Fabrikanten, 1907.

† Hofsäss, J. Gasbelenchtung, 58, 73 (1915).

‡ Ubbelohde and Hofsäss, J. Gasbelenchtung, 56, 1225 (1913).

VIII. Electrical Excitability (fire risk) and Conductance

When woolen fabrics* are agitated in ether or in naphtha an electrical excitation results. Richter† has shown that in each case the exciting liquid (ether or naphtha) assumes a negative charge; the woolen material becomes charged positively. These charges may reach such a value that sparks may result if a workman approaches or touches the material with his hand, and if the proper air and combustible vapor mixture is present, a serious fire may be started. Conflagrations in chemical cleansing establishments have been due to such sparks.

Richter proved that such fires might be prevented by dissolving in the naphtha a small amount (as little as one-twentieth of one per cent) of magnesium oleate. However, the action of this material was not understood.

Richter showed that fires might also result from sparks due to charges generated by the frictional flow of inflammable liquids (ether or naphtha) through narrow pipes either under their own pressure or that of a force pump. In this case also he suggested a practical solution of the difficulty. He found that sparks did not form if the liquids were run through non-conducting earthenware or glass funnels instead of metal funnels, or if a metal funnel seemed to be necessary all trouble was avoided by having a metal chain attached which could make good electrical connection with the earth. If metal funnels were used without "earthing" electrical charges might build up, and, on the approach of a workman, a spark might pass with disastrous results.

Although the practical safe-guards suggested by Richter have been found very satisfactory in the industry, the theoretical explanation of the origin of these electrical excitations has not been entirely acceptable. An attempt was made to explain the transfer of the charge in ether to the metal funnel through which it may be flowing by the relatively high specific conductance of the ether. But it has been shown by means of the apparatus‡ of Fig. 74 that the high differences in potential developed in naphtha may be similarly eliminated by "earthing" though the specific conductance of the naphtha be only $\frac{1}{100,000}$ that of ether.

The naphtha is pushed by carbon dioxide (at 2 atmospheres pressure) from (A) into (B) through the narrow pipe. The vessel (B) rests on amber and is thus in-

* Berichte, **47,** 3239 (1914); Z. f. elektrochemie, **22,** 1, 195 (1916).

† "Die Benzinbrande in den chemischen Waschereien," Oppenheim, Berlin, 1893.

‡ Z. f. chem. Ind., **35,** 166 (1912); **36,** 133 (1913).

sulated. A wire gauze (*C*) is connected with the electrometer (*D*). This allows the measurement of residual charges in the naphtha after "earthing" (*B*). If naphtha or petroleum ether were run into (*B*) under these conditions, charges (up to several thousand volts) would build up but would disappear at once if (*B*) were touched by the hand, or not form at all if (*B*) were touched by the hand as the liquid was being pushed in. This again showed the wisdom of the suggestions of Richter.

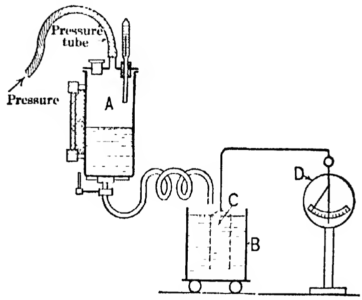


FIG. 74

Probably other factors are concerned in the discharge. Possibly the viscosity has something to do with the development of the charge; for ether and naphtha are mobile liquids, and under equal pressure, would flow more rapidly through small tubes producing a greater excitation than more viscous oils, such as kerosene and lubricating oils. Electrical excitation has not been observed with such more viscous liquids.

Various suggestions have been made to explain the disappearance of the charge in the naphtha on "earthing." It has been thought by some that the mechanical agitation (eddying) in the tank has brought about an instantaneous transfer of the charge. Again some have considered the naphtha when in a state of excitation as comparable to a gas under pressure; when the naphtha is released from the influence of the frictional flow, the charge is immediately communicated to the walls of the receiving tank. Another suggestion has been that by "earthing," the capacity of the system becomes enormously increased thus explaining the drop in voltage. It has however been shown that if the system shown in Fig. 75 is charged at D by means of repeated touching with a rubbed amber rod, even when a charge of 1000 volts has been given, the drop in potential is by no means complete when (B) is "earthed." This has not been satisfactorily explained.

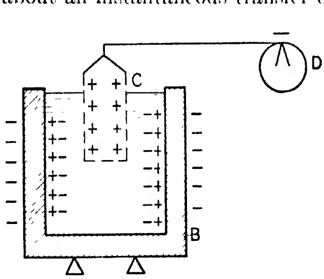


FIG 75.

It must however be remembered that whatever the explanation of the disappearance of the charge the fact remains that all danger of

fire is avoided by " earthing " the metallic pipes, funnels, tanks and receivers, so that any momentary difference in potential is immediately overcome. Calculations (not experimentally verified) have been made on certain assumptions connecting the specific conductance with the time for all but $\frac{1}{10}$ of the charge to disappear. Assuming the maximum voltage to be 3000, since naphtha has a specific conductance equal to 10^{-14}, nine tenths of the charge should have disappeared (it drops to 300 volts) in 39 seconds (with $\kappa = 10^{-15}$, it should take 388 seconds for $\frac{9}{10}$ to disappear) without " earthing; " but on " earthing " the charge disappears instantly.

The tendency to excitation is dependent on the conductance in some way. By an increase in conductance, the fire risk is decreased. Richter showed that in winter, with dry, cold and dust-free air, fires in chemical cleansing establishments due to electric sparks resulted more frequently than in warmer weather. It was shown by Just* that adding magnesium oleate made the naphtha a much better conductor.

Experiments have shown the effects of additions of 96 per cent alcohol and of acetic acid to naphtha of specific conductance equal to 1.4×10^{-15}. By adding 4 volumes of 96 per cent alcohol or 0.1 per cent acetic acid, the conductance was increased 10,000 times bringing it to the magnitude 10^{-11}. With this conductance the time of discharge is cut down to a very short interval.

Not a single case is known of a fire caused by an electric spark arising from vessels which had been sufficiently " earthed." Richter's suggestions have proven to be the most satisfactory way of avoiding fire risk and all later work has simply confirmed his farsightedness.

IX. Specific Heat Capacity

The heat capacity of naphtha is needed for calculating the heating surface of distilling apparatus. See page 43 for method of determination.

American naphtha† has a specific heat capacity of 0.487. Specific heat capacities of a petroleum ether (boiling limits 35° to 40°) at low temperatures have been determined‡:

Specific Heat Capacity	0.588	0.592	0.596	0.601	0.604	0.608
Temperature	− 161.2	− 126.9	− 96.1	− 74.1	− 52.9	− 25.5

* Z. f. elektrochemie, **10**, 202 (1904).

† Graefe, Petroleum, **2**, 523 (1906).

‡ Battelli, Lincei Rend. (3) **16**, [1], 243 (1907); Phys. Z. **9**, 671.

X. Calorific Value

This is of importance in estimating the value of a naphtha for use in internal combustion motors. It is determined in a bomb (see page 49). The heats of combustion of naphtha and of burning oils are given in the table, together with several other values for comparison. See also Table 9, page 57.

TABLE 28

Fuel	Heat of combustion, calories per gram
Naphtha	11,160 to 11,225
Kerosene	11,000 to 11,100
Benzol	10,038
Motor alcohol	5,940
Anthracite	8,000
Bituminous coal	7,000 to 7,500
Air-dried lignite	4,500 to 5,000
Lignite-tar oil	10,400

XI. Aromatic Hydrocarbons

(*a*) **Qualitative.** 1. **Method of Holde.** As much asphalt as will go on the end of a pen-knife, finely powdered and free from inorganic materials is put on a filter paper and the naphtha under examination poured over it. The asphalt should first have been leached free from all soluble matter with petroleum naphtha of specific gravity 0.70 to 0.71. If the filtrate caught in a test tube is free from color, it is considered that considerable quantities of added benzol derivatives are absent; if the filtrate is yellow or brown, benzol or toluol may be assumed to be present. The test depends on the solubility of asphalt in benzol and will detect 5 to 10 per cent of benzol in naphtha.

2. **Method of Dieterich***: The reagent is filter paper saturated with the resin, dragon's blood. This colors benzol and its homologues red; naphtha is not colored. This resin however is also soluble with a red color in ethyl alcohol, methanol, ether, acetone, etc.

3. The commercial benzol may be detected† by means of the indophenin reaction which is given by the thiophen usually occurring in it. (See page 336.)

(*b*) **Quantitative Determination.** 1. This depends on the absorption of aromatic hydrocarbons and olefins (which are present in naphtha only in traces) in sulphuric acid (80 volumes of concentrated, 20 volumes of fuming acid). This method‡ requires further study.

* Motorfahrer, **1915**, 18.

† Bruchhausen, Pharm. Ztg., **58**, 511 (1913).

‡ Kärmer and Böttcher, Gewerbefleiss, 1887.

25 c.c. of naphtha and 25 c.c. of acid are shaken vigorously for 15 minutes in a 75 c.c. heavy-walled flask with a neck 50 cm. long and graduated to 0.1 c.c. After 30 minutes, conc. sulphuric acid (not the mixture) is added till the oily layer is forced into the neck; the volume of the unattacked hydrocarbons is read after an hour's standing or when the volume no longer increases. The difference in the final and original volume allows an easy calculation of the amount absorbed. The method is inaccurate when more than 13 per cent of aromatic hydrocarbons are present.

2. Aromatic nitro-bodies can be extracted with ether after diluting with water the fuming nitric acid solution obtained as in the testing of turpentine (Marcusson, see page 320).

3. See also the method of Edeleanu and Engler for separating aliphatic and other hydrocarbons. See page 112.

XII. Detection of Turpentine and of Pine Oil

The turpentine substitutes found on the market usually consist of the higher boiling portion of the naphtha fraction; the characteristic tests of turpentine are lacking, though the odor may be imitated by the addition of small amounts of turpentine. The addition of the turpentine or of pine oil together with alkali conceals the strong odor of unsufficiently refined naphtha. The additions are recognized as follows (see also pages 318 to 323):

(*a*) Qualitative. If bromine vapor is passed into a test tube containing pure naphtha (or also containing benzol and its homologues) it at once colors the liquid reddish yellow, provided that it contains no exceptionally large amount of unsaturated hydrocarbons; turpentine and pine oil, because of their content of unsaturated terpenes, absorb the bromine without becoming colored. This reaction is used in detecting these substances in naphtha.

Potassium iodide and starch solution are colored by shaking with turpentine or pine oil. Pure naphtha does not give a blue color, though exceptions are known.

Turpentine and pine oil may also be shown to be present by adding one drop of Waller-Hubl's iodine solution to several c.c. of the oil. Pure naphtha is colored red and this color persists undiminished for at least 30 minutes, while with turpentine or pine oil, the color disappears or at least diminishes in intensity. After shaking 5 minutes in the latter case, the color disappears entirely.

(*b*) Quantitatively, turpentine is determined, as on page 319, by means of bromine value, specific gravity, etc.

XIII. Degree of Purity

Crude benzine or naphtha may be slightly yellow; refined naphtha boiling under 150° must be absolutely colorless in a 10 cm. layer. It should not color concentrated sulphuric acid on shaking; when boiled

with water, it should not give up to it any acid substances or impurities of any sort. The refined turpentine substitutes are also colorless in a 10 cm. layer; now and then some samples are found on the market with a pale yellow color.

XIV. Solubility in Alcohol

The solubility of petroleum hydrocarbons in alcohol is greatest in the low-boiling fractions. The naphtha fractions are completely soluble in 96-per cent alcohol; but with more dilute alcohol, such as 94-per cent, the naphtha no longer mixes. See page 128.

XV. Normal Benzine

In precipitating asphalt from dark oils by means of naphtha, it has been found that the results depend on the boiling limits and the origin of the precipitant. See page 105. The amount of asphaltenes precipitated is greater the lower the boiling point of the naphtha and the less the amount of unsaturated compounds it contains.

The Kgl. Materialprüfungsamt Berlin-Lichterfelde-West has since 1903 undertaken the certification of a "normal benzine" (to be obtained from C. A. F. Kahlbaum, Berlin) to be used principally for the determination of asphalt in dark mineral oils.* This must meet the following conditions: specific gravity 0.695 to 0.705 at 15°; boiling limits 65 to 95° (determined by distilling 100 c.c. naphtha in an Engler flask with a 40 cm. LeBel-Henninger column). (See Fig. 76.) The naphtha should be as free as possible from unsaturated and aromatic hydrocarbons; the naphtha is, therefore, tested with the mixture of concentrated and fuming sulphuric acids, not more than 2 per cent of hydrocarbons soluble in the mixture being allowed. The naphtha is also tested as to its ability to precipitate the asphalt in a crude oil from Wietze in comparison with the residue from the previous lot of "normal benzine."

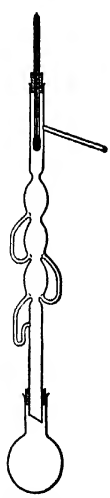


Fig. 76.

* Grundsätze für die Prüfung der Mineralschmieroele, aufgestellt im Jahre 1905 vom Deutschen Verband für Materialprüfungen der Technik, ergänzter Neudruck 1909.

XVI. Specifications for Automobile Benzine (Gasoline)

The material must have been obtained by fractional distillation and should be free from water and all substances likely to injure the motors. Filter paper moistened with the naphtha should not show spots or give a persisting odor. After running through a sieve the naphtha should not separate into fine drops. It should be of uniform composition, not a mixture of high- and low-boiling products. Light naphtha should distill 80 per cent under 100°, all under 130°; heavy naphtha, 50 per cent under 100°, all under 140°. The naphtha must be carefully purified, have no color and only a faint odor. Naphtha for passenger service should have a specific gravity of 0.69 to 0.71 at 15°, for commercial trucks 0.720 to 0.750.

XVII. Turpentine Substitutes

The high boiling naphthas used as turpentine substitutes have flash points over 21° (like kerosene), specific gravities between 0.76 and 0.80 (at times 0.81); their boiling limits may go as low as 90° or as high as 240°, so that they resemble the illuminating oils very much. It is possible to distinguish between these as follows:

In distilling hydrocarbon mixtures, the boiling liquid is always at a higher temperature than the vapors and the difference is greater, the wider the boiling limits of the liquid.* By distilling a Galician petroleum with boiling limits 100 to 300°, a difference in temperature between liquid and vapor of from 35° to 59° was observed; with a kerosene (boiling limits 184 to 252°), a difference of 6° to 8° was recorded.†

Holde uses these phenomena to distinguish between turpentine substitutes and kerosene, since similar differences were observed.

The oil is heated to boiling in an Engler flask, one thermometer being placed in the oil, another in the vapor. It is sufficient to note the differences in temperature at the beginning of boiling, the flask being half filled, distilling a few cubic centimeters of oil.

Turpentine substitute gives a difference of from 5 to 18°, for safety kerosene the difference is 5° to 14°, and kerosene gives differences of from 30 to 45°.

Turpentine substitutes (naphthas) are completely soluble in 3 volumes of 96 per cent alcohol, while all kerosenes, when similarly treated, give mixtures from which separate considerable quantities of

* Graefe, Petrol., **3**, 1128 (1907/08).

† Chemiker Zeitung, **37**, 414, 610 (1913).

oil (shown by cloudiness). This gives a second method of distinguishing the turpentine substitutes from kerosenes. These methods should be further tested.

In several cases where the alcohol test failed, F. Schwarz found the following castor oil test useful:

Twenty cubic centimeters of the sample are shaken at 22° with 10 c.c. of castor oil for 15 seconds. With turpentine substitute (a naphtha) the mixture will be clear after the escape of air bubbles; but the mixture will be cloudy if kerosene was present.

C. Kerosene

I. General

This is the fraction which distills between 150° and 300° and which has been purified by treatment with sulphuric acid. The boiling limits are not to be taken as fixed, for generally small amounts of components boiling under 150° and some boiling over 300° are present. Lamp oils are also prepared which boil no higher than 275°. A good lamp oil should have a flash point reasonably high (for Germany 21°) and should burn well in a standard burner (in Germany generally the Kosmos burner), without smoke, soot or odor.

II. Color Tests

A normal kerosene should be transparent in a 10 cm. layer or should have at the most only a faintly yellow color; the expensive grades (such as water-white, Kaiser-oel) are as clear as water. Exposed to sunlight all kerosenes get yellower without affecting their combustibility.* In the market, it is sold according to color. The colorimeters of Wilson, of Stammer and of Saybolt allow the determination of certain normal tints.

As long as only American kerosene came on the market, the color test was of great importance; since, however, other oils from other sources are on the market and these are satisfactory in spite of their yellow color, the color tests have lost in importance.

(*a*) **Colorimeter of Stammer.** The instrument is to be obtained from Schmidt and Haensch, Berlin, in the form used at Baku (Fig. 77). In the Stammer apparatus, the thickness of a layer of oil is adjusted until it has the same color as a plate of uranium glass of definite thickness and color. The Stammer apparatus requires the following length of column of oil for the usual grades:

* Mitteilungen, **21**, 52 (1903).

Standard White	50 mm.
Prime White	86 5
Superfine White	199.5
Water White	300 to 320

z is an immovable tube which has a colored glass plate at the top. *c* is a movable cylinder containing the sample of kerosene; in this the tube *t* dips more or less according to the height of the cylinder. The light passes from a mirror *p* through *z* and *c* through two prisms to the eye-piece *o* The height of the column of petroleum measured on the scale *m* is altered until the color in the two tubes is the same.* To prevent the action of metal on the kerosene, Engler recommends the use of a glass cylinder.

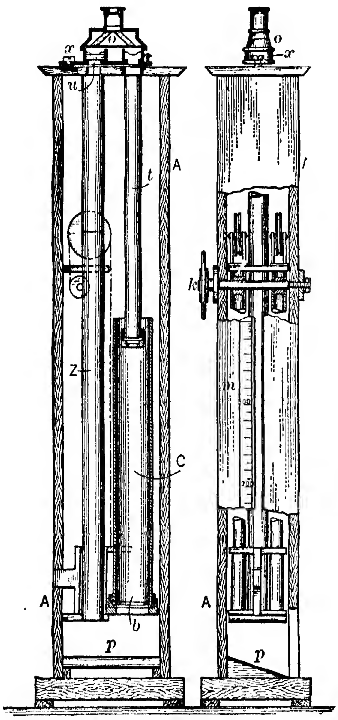


FIG. 77

(*b*) **The Colorimeter of Wilson.** This can be obtained from W. Ludolph, Bremerhaven. This has the widest application especially in England and Russia. In the Wilson-Ludolph apparatus, the color of a certain layer of oil is compared with different glass plates of different tints.

Two brass tubes *b* are fastened to the cover of a wooden cabinet the cover of which may be adjusted to any angle. The glass tubes containing the kerosene and the glass plates are placed inside these tubes. (Figs. 78 and 79.) Both tubes can be closed tightly by a cap screwing on over a glass plate. Reflected light is sent into the tubes from a mirror fixed in the bottom of the box as in the colorimeter of Stammer. Four glasses are supplied with each instrument, each representing one of the standard shades of color, the lightest being water white, the darkest, standard white.

To determine the color, one of the tubes is filled with the oil and introduced into the instrument and compared with the various standard glasses. As a matter of fact, the color is rarely exactly that of one of the four. But the grade given is always the poorer; if the color is between water white and superfine white, it is taken as superfine white, etc. At Baku, however, it is customary to classify in fractions of the different grades.†

* Ding. Poly. Jour., **264**, 287.

† Quitka, Arbeiten der K. Russ. Tech. Gesellschaft, 1889–1891; Kwjatkowsky and Rakusin, Praktische Anleitung zur Verarbeitung der Naphtha, Berlin, 1904.

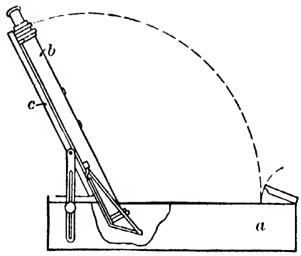


FIG. 78.

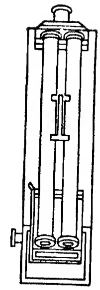


FIG. 79.

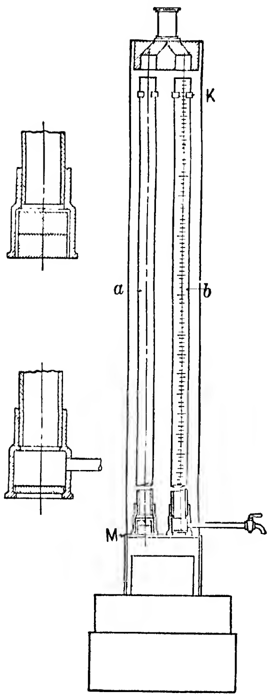


FIG. 80.

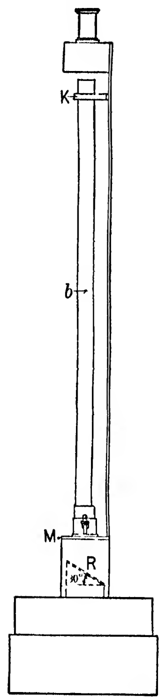


FIG. 81.

The color of the Baku oil is generally between grades 2 and 3; the fractions are determined as follows:

If to get the same color in the two tubes, glass plate No. 2 is on the tube filled with oil while glass plate No. 3 is on the empty tube, then the kerosene is of grade

2.5. According to whether it is darker or lighter than plate No. 3 it is called grade $2\frac{3}{4}$ or $2\frac{1}{4}$. When glass plate No. 1 is placed on the filled tube and glass plate No. 3 on the empty, the grade is also called $2\frac{1}{4}$.

As is stated in the Official Russian Regulations the glass plates of the different instruments vary in intensity and density; in order to obtain comparative results, in spite of these differences, the colors of the various grades of American kerosene were given in terms of acidified solutions of potassium chromate of different concentrations by the Baku Section of the Imperial Russian Technical Society.

(*c*) **Colorimeter of Saybolt** (Figs. 80 and 81), used in the United States, depends on the same principle as that of Stammer. The color of the kerosene is compared with that of a glass plate of uranium glass, the height of the oil being adjusted by running out some through the cock at the side.

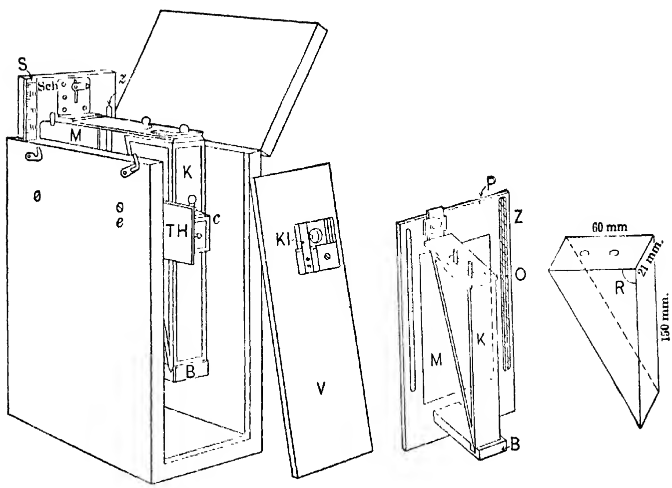


Fig. 82.

The two glass tubes (*a*) and (*b*), (*a*) empty, rest on the metal plate (*N*) through which two circular holes allow the passage of light from the reflector (*R*). In the receptacle at the bottom of (*a*) may be placed one or two uranium glass plates; the tube (*b*) contains a colorless glass disk.

(*d*) **The Colorimeter of Hellige,** depending on the same principle as that of Wilson, has been found useful.* Fig. 82.

* Petroleum, **10**, 725 (1914).

The kerosene is placed in a vessel (*c*) (10 × 19 × 51 mm. at top, 48 mm. at bottom); it is compared in color with a normal solution (0.06 g. potassium bichromate in one liter of water) which is placed in the receptacle (*k*) (60 × 150 × 21 mm.). The back of the apparatus (Sch) is moved until both fields of observation show the same intensity of light. The position on the scale is the "Hellige number."

The following gives a comparison of colorimeter values:

TABLE 30

Grade of kerosene	Wilson	Stammer	Hellige
Standard White	Grade 4	50 mm.	75
Standard White	Grade 3½	68	55
Prime White	Grade 3	86 5	43
Prime White	Grade 2¾	115	32.5
Prime White	Grade 2½	143	26
Prime White	Grade 2¼	172	22
Superfine White	Grade 2	199	19
Superfine White	Grade 1½	255	15
Water White . .	Grade 1	310	12

The Stammer values may be obtained from the "Hellige number" (H) as follows:

$$S = \frac{3733.5}{H}$$

III. Specific Gravity

Determination. See page 2.

To reduce the values observed at room temperatures to the normal (15°), the following corrections of D. Mendelejeff are to be applied to Russian oils:

TABLE 31

Specific gravity	Decrease for 1°
0 760–0 780	0 000,790
0 780–0 800	0 000,780
0 800–0 810	0 000,770
0 810–0 820	0.000,760
0.820–0 830	0 000,750
0 830–0 840	0 000,740
0 840–0.850	0 000,720
0 850–0 860	0 000,710

The specific gravity of kerosene will rise, as shown by Engler* for

* Berichte, **43**, 405 (1910).

synthetic kerosene from train oil; on long standing, such material will polymerize even in closed bottles.

IV. Viscosity

In order that a kerosene may burn normally, it is necessary that the wick shall supply enough oil to the flame. The rise of the oil in the capillaries is determined by the surface tension that the oil exerts in the capillaries. The viscosity of the kerosene opposes the rise by increasing the resistance in the capillaries.* Stepanoff gets the following relationship between the amount of oil M, the capillary constant α and the viscosity Z

$$M = \frac{\alpha^2}{Z}.$$

The specific gravity of the oil is of negligible influence on the amount of oil raised. The capillary constants of the different illuminating oils are about 3 mg./mm. and vary so little that they may be considered practically constant. The viscosity as determined in the kerosene viscosimeter (described in the following) varies from 1.11 to 1.80 (water at 20° = 1; 100 c.c. water have an efflux time of 200 seconds).

The Engler viscosimeter (see page 16) for lubricating oils is not suited for kerosene, because the diameter of the exit being so great, the time of outflow is very short and the differences shown by the oils become too small to be of practical value. The apparatus† constructed by Ubbelohde at the suggestion of Engler may be used for naphtha, kerosene and other mobile liquids, but not in the place of the Engler viscosimeter for lubricating oils. It may be used, instead of the Engler apparatus, in the testing of steam cylinder oils at high temperatures. It must, however, be remembered that the viscosity measured on the Ubbelohde apparatus is not identical with that determined in the Engler apparatus; the Engler degrees are much smaller.

V. Cold Test

Kerosene which is exposed to cold weather in the open should remain liquid at low temperatures and should show complete liquidity in the wick; it should remain liquid at − 10°.

* Ubbelohde, Petrol., **4**, 861 (1909); Engler, Lewin and Stepanoff, Grundlagen der Lampentheorie, 1906.

† The apparatus may be obtained from Sommer and Runge, Berlin, Friedenau, Benningsenstrasse.

The apparatus of page 35 is used for this; after a preliminary experiment, the samples are kept for 1 hour at the temperature in question, taking care to prevent disturbance of the material. Only fresh samples (which have not previously been cooled) are to be used, otherwise the results are uncertain. In more careful work, the cold test of the residue remaining on heating the kerosene to 300° must be made.

If the kerosene was not carefully distilled or if the crude oil contained much paraffin (Boryslaw oil) it will show at − 10° a separation of paraffin. Russian kerosene is still clear at − 20°, while a sample of Nobel kerosene was still liquid at − 70° (it might be a good lubricant for low temperatures). Kerosene, containing paraffin, probably in the form of a colloidal solution, has, when examined at room temperature in the ultra-microscope, an entirely different appearance from kerosene,* free from paraffin.

VI. Flash Point

This is a criterion of the inflammability of the kerosene. The open testers were formerly much used, but have been largely given up, because of the errors involved; the closed form is now generally used (see page 42). It is stated, however, that the liability of a kerosene to explode in lamps is not exactly determined by the Abel-Pensky test, but should be determined by explosion tests in a eudiometer† (see page 120).

The temperature at which, in the ordinary lamp reservoir, explosive mixtures form, is, according to Engler,‡ about 8° higher than the corresponding temperature in the Abel tester. He, therefore, held 23° as a minimum for the flash point, in view of the fact that it had been shown by the German Bureau of Public Health and Hygiene that the temperature of the oil in the reservoir was 5° higher than the room temperature (at 20°), and assuming an average temperature of 28° the above value 23° was suggested. However, the legal (German) flash point was fixed at 21°.

(*a*) **The Abel Tester.** This (Fig. 83) consists of the water bath *W*, the kerosene holder *G*, and the cover which supports the thermometer and a mechanism for running the ignition apparatus. The water bath is fitted with a funnel *C*, an overflow pipe and a thermometer t_2. The copper vessel soldered into the middle of *W* forms a cavity into which the vessel *G*, after it has been filled to the mark h_1 with the oil to be tested, is placed. In one position the holes in the cover and the slide corre-

* Ztschr. f. Chem. u. Ind. der Kolloide, **2**, 270 (1908).

† Chem. Ztg., **29**, 741 (1905).

‡ Chem. Ind., **1882**, 106.

spond, in another, the holes are covered. The knob b is wound up to start the driving mechanism T; if the lever h is pushed down, the mechanism turns the slide. At the same time the small lamp a fixed on a horizontal axis, sinks so that when the holes of the cover are entirely open, a small test or pilot light is thrust for two seconds into the space filled with kerosene vapors and air.

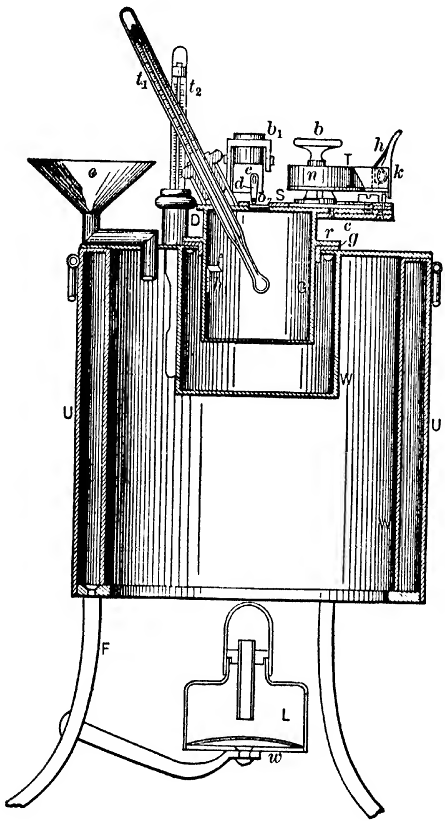


FIG. 83.

(*b*) **The Testing.** The kerosene which has been put into the vessel G is cooled 2° below the temperature necessary to start (the testing is started at different temperatures according to the barometric height, Table 32). The cooling can be done directly in the vessel G before it is carefully lowered into the water bath W. The kerosene should not wet the walls of the vessel above the mark.

The pilot light flame should be as large as the white bead on the cover; a cotton wick saturated with kerosene is used. After the bath has been warmed to 54 to 55° and the alcohol lamp is extinguished, the pilot light is thrust in every half degree. Before the actual flash point is reached, the test flame will be seen to increase with a halo-like effect when dipped towards the oil. The true flash point is the temperature at which a lightning-like, large blue flame spreads over the entire free surface of the oil (even if the pilot light is not extinguished by the flash).

(*c*) **Repetition of the Test.** Before repeating, the cover must cool and all traces of oil must be removed from it, from the vessel and the openings of the slide and cover. Before introducing the vessel into the water bath, the water is again heated to 55°. If the second determination varies from the first by not more than 0.5°, the average is taken as the apparent flash point, the temperature at which under the existing conditions, the flash will occur. If the second result varies more than 1°, the determination is repeated; if the three vary no more than 1.5° the average is taken.

TABLE 32

With the barometer at mm. inclusive	The testing is begun at °C.	With the barometer at mm. inclusive	The testing is begun at °C.
685–695	+ 14.0	736–745	16 0
696–705	14 5	746–755	16.5
706–715	15 0	756–765	17.0
716–725	15.5	766–775	17 0
726–735	16 0	776–785	17 5

(*d*) **Calculation of the flash point at 760 mm.** The values are taken from the table (Table 33) or interpolated in case the values are not given.

Example: Barometric height 742 mm.; 740 is the nearest.

First flash-point determination was	19 0
Second	20 5
Third	19.5
Average value	19.7

In the column for 740 mm. the nearest value is 19.8; in the same line for 760 mm. the value would be 20.5. This last is the flash point of the kerosene referred to normal atmospheric pressure. Since it is under 21° (the minimum for Germany), it is acceptable.

For oils flashing above 50° hotter or boiling water must be used in the bath; for oils with flash points between 60° and 80°, the space between the kerosene container and the water bath is filled with a mineral machine oil. The water bath is then heated 15° above the flash point of the kerosene as determined in a preliminary experiment. In Russia official regulations require that all oils from the Baku region flashing under 85° are to be tested by the Abel apparatus; for higher flashing oils, the Pensky tester is used.

A comparison carried out in the Materialprüfungsamt showed the flash point in the Pensky apparatus, in which the rate of rise up to 50° was 1 to 2 degrees per minute, at 70°, 1 to 4 degrees per minute, to be 0.4 to 0.8° lower than in the ordinary Abel apparatus. The Pensky apparatus, therefore, with careful heating is suited for the testing of mineral oil distillates between 50° and 100°.

VII. Burning Point

The burning point, or the temperature to which the oil must be heated in order that the oil will continue to burn uninterruptedly when a small flame is brought near, can be determined in an open tester. See page 42.

A thermometer fastened to a ring-stand dips into an open kerosene container. Without touching the surface, a test flame is applied for 2

TABLE 33

Recalculation of the Observed Point at Atmospheric Pressure to the Flash Point at Normal Pressure

Barometric height in millimeters

650	655	660	665	670	675	680	685	690	695	700	705	710	715	720	725	730	735	740	745	750	755	760	765	770	775	780	785
Flash point																											
15.5	15.6	15.7	15.8	15.9	16.1	16.2	16.4	16.6	16.7	16.9	17.1	17.3	17.4	17.6	17.8	18.0	18.1	18.3	18.5	18.7	18.8	**19.0**	19.2	19.4	19.5	19.7	19.9
16.0	16.1	16.2	16.3	16.4	16.6	16.7	16.9	17.1	17.2	17.4	17.6	17.8	17.9	18.1	18.3	18.5	18.6	18.8	19.0	19.2	19.3	**19.5**	19.7	19.9	20.0	20.2	20.4
16.5	16.6	16.7	16.8	16.9	17.1	17.2	17.4	17.6	17.7	17.9	18.1	18.3	18.4	18.6	18.8	19.0	19.1	19.3	19.5	19.7	19.8	**20.0**	20.2	20.4	20.5	20.7	20.9
17.0	17.1	17.2	17.3	17.4	17.6	17.7	17.9	18.1	18.2	18.4	18.6	18.8	18.9	19.1	19.3	19.5	19.6	19.8	20.0	20.2	20.3	**20.5**	20.7	20.9	21.0	21.2	21.4
17.5	17.6	17.7	17.8	17.9	18.1	18.2	18.4	18.6	18.7	18.9	19.1	19.3	19.4	19.6	19.8	20.0	20.1	20.3	20.5	20.7	20.8	**21.0**	21.2	21.4	21.5	21.7	21.9
18.0	18.1	18.2	18.3	18.4	18.6	18.7	18.9	19.1	19.2	19.4	19.6	19.8	19.9	20.1	20.3	20.5	20.6	20.8	21.0	21.2	21.3	**21.5**	21.7	21.9	22.0	22.2	22.4
18.5	18.6	18.7	18.8	18.9	19.1	19.2	19.4	19.6	19.7	19.9	20.1	20.3	20.4	20.6	20.8	21.0	21.1	21.3	21.5	21.7	21.8	**22.0**	22.2	22.4	22.5	22.7	22.9
19.0	19.1	19.2	19.3	19.4	19.6	19.7	19.9	20.1	20.2	20.4	20.6	20.8	20.9	21.1	21.3	21.5	21.6	21.8	22.0	22.2	22.3	**22.5**	22.7	22.9	23.0	23.2	23.4
19.5	19.6	19.7	19.8	19.9	20.1	20.2	20.4	20.6	20.7	20.9	21.1	21.3	21.4	21.6	21.8	22.0	22.1	22.3	22.5	22.7	22.8	**23.0**	23.2	23.4	23.5	23.7	23.9
20.0	20.1	20.2	20.3	20.4	20.6	20.7	20.9	21.1	21.2	21.4	21.6	21.8	21.9	22.1	22.3	22.5	22.6	22.8	23.0	23.2	23.3	**23.5**	23.7	23.9	24.0	24.2	24.4
20.5	20.6	20.7	20.8	20.9	21.1	21.2	21.4	21.6	21.7	21.9	22.1	22.3	22.4	22.6	22.8	23.0	23.1	23.3	23.5	23.7	23.8	**24.0**	24.2	24.4	24.5	24.7	24.9
21.0	21.1	21.2	21.3	21.4	21.6	21.7	21.9	22.1	22.2	22.4	22.6	22.8	22.9	23.1	23.3	23.5	23.6	23.8	24.0	24.2	24.3	**24.5**	24.7	24.9	25.0	25.2	25.4
21.5	21.6	21.7	21.8	21.9	22.1	22.2	22.4	22.6	22.7	22.9	23.1	23.3	23.4	23.6	23.8	24.0	24.1	24.3	24.5	24.7	24.8	**25.0**	25.2	25.4	25.5	25.7	25.9

seconds after every rise of one degree. Or after the flash point has been determined by the Abel tester, the cover is taken off, the tests being then made with a regular blowpipe flame. The test-flame must not be allowed to remain too long near the surface before the start of the burning. This determination is of very little importance in the case of kerosene or other mineral oils, and has only to be considered in estimating the inflammability of an oil with especially low flash point.

VIII. Fractional Distillation

This is carried on with the Engler-Ubbelohde glass apparatus with continuous operation (see page 99). The following resolutions were passed by the International Commission on the Analysis of Petroleum Products: The barometric height is to be recorded and the correction for protruding stem is to be considered (thermometers of like dimensions to be used). (See page 101.) The condenser tube must be perfectly dry. The beginning of boiling is the temperature at which the first drops fall from the side-tube of the Engler flask. The limits of the fractions caught are to be exactly divisible by 25. Generally the volume of the fractions is determined, the portion distilling over 300° and remaining in the flask is weighed. In exact analysis, the fractions are weighed, as is also the quantity taken for examination.

Fractional distillation is used in connection with the determination of candle power and content of unsaturated hydrocarbons in estimating the value of a kerosene. But the distillation test does not have any direct connection with the candle power of a lamp oil. The candle power depends to a large extent on the kind of burner. Only a burning test under actual conditions of use will give conclusive results.

In general the following points should be kept in mind: Distillation should not begin below 110°. Considerable amounts boiling over 300° cause poor burning especially in a test of some duration. In the best lamp oils 90 per cent will distill between 150 and 300°, with not more than 5 per cent distilling above 300°.

IX. Purity

(*a*) **Sulphur.** Since Ohio oil with its high content of sulphur has been refined into illuminating oil, the analysis of kerosene has included also the determination of sulphur, since a high sulphur content gives rise to an unpleasant odor on burning. Graefe* has shown that sulphur, in so far as it is not present as a derivative of sulphuric acid, does not

* Petrol, 1, 606 (1905).

affect the illuminating power of the oil. Esters of sulphuric acid, however, on burning cause a carbonization of the wick and, therefore, decrease the candle power.

The method of Carius for the determination of sulphur (see page 224) is not suited for kerosene, since even a poor quality of oil contains not more than a few hundredths of a per cent and the methods do not allow the use of large amounts of material.

1. The determination may be made by combustion with oxygen in a bomb (see page 77) as is frequently done in American laboratories.

2. Very useful is the method worked out at the suggestion of Allen by Heussler and Engler;* this can also be used for the determination of sulphur in illuminating gas.

The method depends on the burning of the kerosene in a small lamp (Fig. 84) and suction of the products of combustion into the absorption vessel containing potassium hypobromite solution (made from bromine and a 5 per cent solution of potassium carbonate or hydroxide and decolorized by aeration). The sulphuric acid thus formed is precipitated as barium sulphate and weighed in the customary manner.

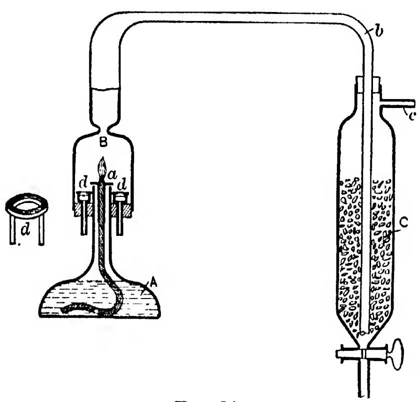


Fig. 84.

The absorption liquid is easily obtained free from sulphur. It oxidizes the sulphur dioxide of the products of combustion. 20 c.c. are necessary to fill the apparatus. The small lamp A is fitted with a wick and a wick holder. The chimney is continued in the fused-on glass tube b which reaches to the bottom of the absorption vessel C which is filled with glass beads and the absorption liquid. In the neck of C is the tube c which is connected with the water-jet suction pump. A cork at the top makes the apparatus air-tight. The chimney B is fastened to the neck of A by means of corks. The metal ring is so fastened in the cork that the air entering the two tubes distributes itself through the entire circular space and uniformly to the flame through the wire gauze on top. The small vessel for the kerosene contains about 100 c.c. of oil and is purposely made broad so that there will not develop too great a difference in level during the burning; this helps to keep the burning uniform. The distance from flame to bottom is 9 cm. After igniting the filled and weighed lamp, the air is sucked through so that the flame burns without smoking.

* Chem. Ztg., **20**, 197 (1896).

Since the laboratory air often contains sulphur, the two tubes *d* are connected by a *T*-tube with a tube leading to the open air, thus insuring a clean supply. In five hours, during which it requires no attention, about 10 to 12 grams of oil will burn; this is enough. The weight is again taken. The stopcock is then opened and the liquid run out; to rinse, 20 c.c. of water are added, air is sucked through and the water again run off. This is repeated several times. In this way about 100 c.c. of liquid are obtained containing only 1 gram of potassium salt. In this the sulphur is determined by weighing as barium sulphate.

After washing, the apparatus is again ready for use and can at once be refilled with absorption liquid. It is not necessary to remove the chimney-tube *Bb* from the vessel *C*.

Of importance seems to be the suggestion of F. Schulz* to determine the sulphur by volumetric titration. The evolved sulphur dioxide is absorbed in previously neutralized hydrogen peroxide (60 c.c. of 1.5 per cent solution), the sulphuric acid formed being titrated with $\frac{N}{10}$ sodium hydroxide in presence of methyl orange.

3 In another method used in the United States† the oil is burned in an Erlenmeyer flask of 25 c.c. capacity, using a small glass tube as a wick-holder (Fig 85). In the vessel (*D*) are placed glass beads drenched with 10 c.c. of a solution of sodium carbonate (1 c.c. ≏ 0.001 gram of sulphur). Suction is applied at (*E*). After weighing, the lamp is lighted and placed under the tube (*B*). The acidic vapors react, the excess of carbonate solution being titrated with standard sulphuric acid in the presence of methyl orange.

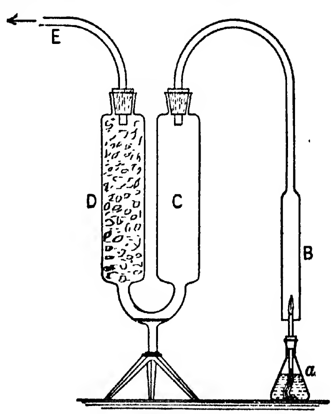


FIG. 85.

Conradson has pointed out that in these lamp combustion methods the sulpho-acids and sulphates occurring in imperfectly purified oils escape detection if the oil is not completely burned. He suggests burning a large amount and also recommends examining the wick.

To determine total sulphur the method of Rothe is suggested. Page 78.

According to Kissling and Engler,‡ Kaiser oil contains 0.01, astral oil 0.02, ordinary Pennsylvania oil 0.027 to 0.029, Russian 0.027 to

* Petroleum, **8**, 585 (1912).
† Engler-Höfer, **4**, 65.
‡ Chem. Rev., **13**, 158 (1906).

0.030, Galician 0.039 to 0.062, Ohio oil 0.04 to 0.05, Alsatian 0.06 to 0.068 per cent of sulphur.

A good kerosene should not contain more than 0.03 per cent of sulphur. According to Graefe* the sulphur content serves as a test for solar oils from brown-coal tar, which may contain 0.5 to 1.0 per cent, on the average 0.8 per cent of sulphur. See page 301.

(*b*) **Esters.** According to Heussler and Dennstedt† the cause of the carbonization of the wick is the sulphuric acid derivatives formed during the refining process, these burning with the formation of sulphuric acid.

To demonstrate the presence of these, lamp oil is heated in a paraffin bath at 140° with anilin. At this temperature, in the presence of these materials a cloudiness develops, due to the precipitation of anilin sulphate. The precipitated salt is decomposed with water and the separated sulphuric acid detected in the aqueous solution.

(*c*) **Acidity.** 1. **Mineral Acid.** On shaking 100 c.c. of kerosene with 10 c.c. of distilled water several drops of 1/1000 methyl orange being added, a red color should not develop.

2. **Organic Acid.** 100 c.c. of kerosene in 100 c.c of a freshly neutralized solution of 4 parts of ether, 1 part of 95 per cent alcohol and 1 drop of phenolphthalein are shaken in a glass-stoppered cylinder with 1 drop of N 10 sodium hydroxide. If the kerosene is neutral, the red color will not disappear.

(*d*) **Presence of Salts of Naphthenic and Sulpho Acids.** Qualitatively these substances, which decrease the burning power of the oils, can be extracted from the kerosene by shaking with dilute NaOH and precipitating the acids by acidifying with a mineral acid.

300 c.c. of kerosene are warmed to 70° on a water bath with 18 c.c. of NaOH of specific gravity 1.014 in a 500 c.c. flask and vigorously shaken for 1 minute. The aqueous solution is separated in a separatory funnel and, after filtering, divided into two parts. To one part, conc. hydrochloric acid is added from a dropping funnel till litmus or methyl orange is turned red. Then, to the second portion is added the same number of drops and, immediately after acidifying, it is examined to see if one can see through it well enough to read small type; if the type is visible, the sample is free from considerable amounts. If the type is not visible, the acid value (see above), or, if no free acid is present, the ash is determined according to (*e*). A positive test with the NaOH does not always mean that such salts are present. Exposure to light may make the kerosene acid enough to give a positive test; even the best grades (water white) will change in this way and in color.

(*e*) For determination of Ash see page 73. A good kerosene should not contain more than 2 milligrams per liter.

* Chem. Rev., **12**, 271 (1905).

† Ztsch. für. angew. Chem., **17**, 264 (1904).

(*f*) **Turbidity.** On long standing kerosene may become turbid; it is due to presence of sodium salts of sulphuric or other sulphur acids. These are separated by filtration and examined.

X. Unsaturated Hydrocarbons

Many kinds of kerosene, especially Galician and Rumanian oils, contain unsaturated hydrocarbons of the olefin, benzene and partially hydrated cyclic series. According to Kramer and Böttcher and experiments of Weger* the amount of unsaturated hydrocarbons (soluble in conc. sulphuric acid) (see page 125) is an important test for the estimation of the value of a kerosene. The hydrocarbons mentioned are said to cause a red coloration of the flame, and, therefore, with equal intensity of flame, the flame rich in unsaturated bodies appears darker. This is, however, only the case with lamps constructed for American kerosene. Borneo or Bustenari oils, which burn poorly with ordinary lamps, after removal of the aromatic derivatives, are said to be as good in lighting power as the best American oils. See also pages 111 and 125.

XI. Solubility in Absolute Alcohol

At ordinary temperature kerosene is easily soluble in two volumes of absolute alcohol, generally also in less. According to Aisinman† all crude-oil fractions up to a specific gravity 0.835, in other words, most petroleum products, mix in all proportions with alcohol. Kerosene is not completely soluble in three volumes of 96 per cent alcohol. See page 128.

XII. Burning Test and Lighting Value

The burning tests are best carried out with a Bunsen photometer using a Lummer-Brodhun photometer box.‡

(*a*) **Photometer.** To determine the candle power of kerosene, the precision photometer of the Physikalisch Technischen Reichsanstalt is used in the Kgl. Materialprüfungsamt (Fig. 86).§

Two steel rods covered with hard rubber are mounted on three cast-iron supports; on these are placed three movable carriages, I, II, III, each running on

* Chem. Industr., **1905**, 24.

† Ding. Poly. Jour., **297**, Heft 2 (1895); Chem. Rev., **4**, 161, 176 (1897).

‡ As recommended by the "Vereinigung der Gas- und Wasser-fachmänner Deutschlands" for the testing of illuminating gas.

§ The bench is supplied by Schmidt and Haensch, Berlin; in factory laboratories cheaper and simpler instruments are used, these being made by Elster, Weber, and others.

three rollers. Each carriage has in its center a vertical steel rod movable up and down by means of T and clamped by t. On one is placed the standard lamp N (a standard incandescent or a Hefner amyl acetate lamp), on another carriage is placed the Lummer-Brodhun photometer box LB, and on the third the light to be measured. Each carriage has a clamping arrangement and an index by means of which its position on the 2.5 meter scale is determined (this scale carries mm. graduations). The screens B are of aluminum foil covered with dark velvet so that only the light from L and N strikes LB. The measurement is made by moving the carriage LB until the light intensities from N and from L appear equal in LB. (An optical arrangement allows very accurate comparison in LB.) After determining on the scale the distances N to $LB = a$ and L to $LB = b$, the intensity of light is calculated to be

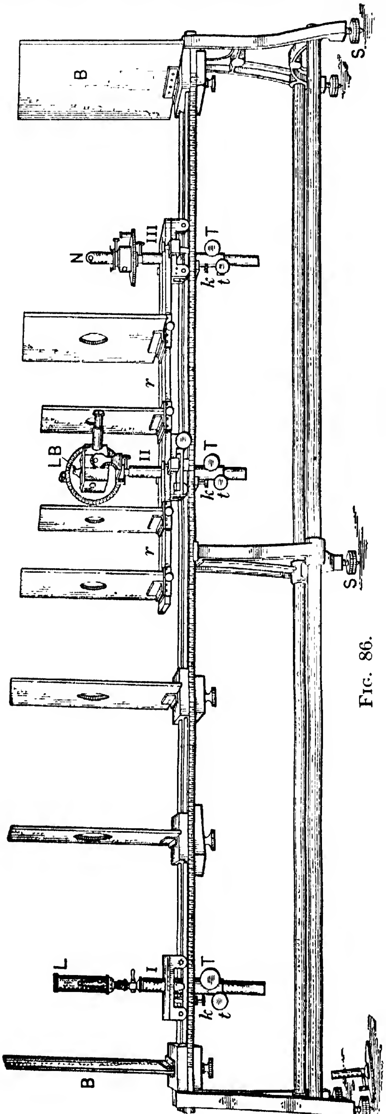


Fig. 86.

$$\frac{L}{N} = \frac{b^2}{a^2};$$

but since N, in case amyl acetate was used, equals 1,

$$L = \frac{b^2}{a^2}.$$

In Fig. 87a is shown the optical arrangement of the Lummer-Brodhun photometer box. The sources of light illuminate each a side of the screen (S). The oblique rays (a) and (b) are reflected from the mirrors (A) and (B) then pass through (rays d), or are reflected from (rays c), the hypotenuse surfaces of the double prism, and after passing the lens produce an image as shown in Fig. 87b.

The double prism consists of two right-angled prisms with hypotenuse surfaces against each other. On the left one are etched (or blasted) small depressions. At these points the rays

(c) are totally reflected, the unetched surface allows the passage of the rays (d). The observer sees the depressions illuminated from the right, the unetched portion from the left side of the screen, and can judge of the differences in light intensity. The photometer box is moved till the trapezoids (r_1) and (l_1) (Fig. 87b) seem equally bright, or until there is no visible line separating the two halves of the field of vision.

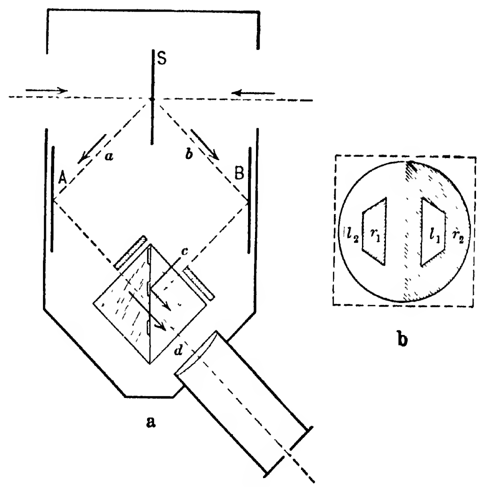


Fig. 87.

(b) **Method of Testing.*** 1. The construction of the lamp influences the candle power of the material and its ability to burn. Especially important are, the method of supplying the air, height of the chimney constriction above the burner and the general form of the rest of the chimney, the kind of wick, etc. The lamp must be carefully chosen to represent a practical use of the oil. Comparisons of kerosenes must, of course, be made only by using the same lamp. The new wick to be used must be previously dried at 105° and, while still warm, saturated with the kerosene. After ignition it is pressed together in the wick-holder until there are no peaks in the flame. The oil reservoirs of the photometer lamps should be as wide as possible in order that the difference in level between the rim of the burner and the level of the oil should change as little as possible. 700 c.c. of oil are to be put into the reservoir. The lamp generally used is a 14 mm. circular burner. For oils which require a large supply of oxygen for complete combustion, as, for example, naphthene-rich Russian or Galician oils, as well as those rich in unsaturated or aromatic hydrocarbons, the "reform" burner of Schuster and Beer is to be used. The dimensions of the Kosmos burner chimney are: 26 cm. height, the constriction to be 5 cm. high and 2.5 cm. wide.

2. **Adjusting the Height of the Flame.** To develop completely the illuminating power of several kinds of kerosene (especially Nobel kerosene) a small flame must be used at the beginning of burning. For the first five minutes the flame is to be about as high as the constriction, after which it is gradually increased in height until a

* See also Eger, Die Distillationsprodukte des Erdöls in ihrer Verwendung als Leuchtöl, Chem. Rev., **6**, 81 (1899); Albrecht, Ueber den Brennwert des russischen Petroleums, ibid., **5**, 189 (1898); Lunge-Berl, Chem.-Technische Untersuchungsmethoden, 6te Auflage, Bd. III, 320; Deutsche Verbandschlüsse, **1909**; Stepanoff, Grundlagen der Lampentheorie, Stuttgart, **1906**; Prössdorf, Brennversuche; Petroleum, **3**, 231 (1907).

larger flame causes smoking or unsteadiness. If the flame has remained at its maximum for 15 minutes before taking the first photometer reading, it will remain the same during the rest of the test. The constriction of the chimney is to be so chosen, or the chimney is to be so placed, that the maximum candle power will develop. The height of the flame can be determined exactly by an arrangement with a small lens and upright scale (Fig. 88); in more exact measurements a cathetometer and telescope are used.

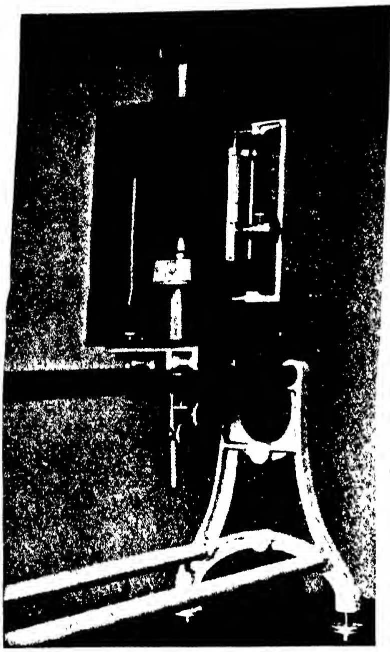


FIG. 88.

3. **The Candle Power** is determined only when the maximum height has been reached after at least 30 minutes burning (in more accurate work, only after 1, 2, 3, 4, 5 and 6 hour's burning).

The poor illuminating power of those kerosenes containing a large amount of material boiling over 270° shows itself only after prolonged burning; the candle power of such an oil will decrease decidedly after several hours.

4. ***The Amount of Kerosene*** used is determined by weighing the lamp before and after the test and, in exact work, after each measurement. The result should include not only a statement of the average candle power and the total quantity consumed, but also the consumption per candle-hour, and should state if an odor developed and also the length and weight of wick carbonized.

5. In very careful work, that portion of the oil remaining in the reservoir after one-half of the oil in the lamp has burned, is distilled in order to determine if any change in composition has taken place.

6. In Germany the **standard** is the Hefner-Alteneck amyl acetate lamp, the flame of which is adjusted to a height of 40 mm. The working room is to be well ventilated, otherwise the light emitted will vary. The difficulty in controlling the height of the flame, the effect of the humidity and changing temperature of the air and the sensitiveness of the flame to draughts make the use of the amyl acetate lamp difficult and time consuming. With the electrical standard lamp these difficulties disappear. If electric current with suitable apparatus is available, the normal electric incandescent of 10 Hefner candle power is used, the candle power of this being compared from time to time with the Hefner standard.

The United States Bureau of Standards has determined and defined an international standard in order to facilitate the calculations for international use. This has been accepted by England, France, and the United States but was not accepted

by Germany although the great necessity for such a standard is recognized. The relations are as follows:

One international candle equals......	0.104 Carcel units
One international candle equals......	1.11 Hefner units
One international candle equals......	1.0 American candle
One international candle equals.... .	1 0 Bougie décimale

7. **Physical and Chemical Tests** (without a practical burning test) can give information regarding the combustibility of the oil only in case the source of the oil is known with certainty.

8. **Example.** On a 14 mm. Stobwasser burner American water-white kerosene showed after 1 hour 1 .8 candle power, after the third hour, 18.7 Hefner candle power: for Nobel kerosene (Caucasus) the corresponding values were 14.9 and 14.7. The decrease in candle power which takes place with practically all oils to a greater or less degree is said to result from a fractionation of the oil in the wick. On a "patent reform burner" water-white kerosene gave 21.7 and 21.3 Hefner candle power, Noble kerosene 18.2 and 18 2. The consumption per hour and Hefner candle for the Stobwasser burner was 2.81 grams, for the reform burner 2.71, in both cases with water-white kerosene; with Nobel kerosene the values were 3.24 and 2.90 grams. Rumanian oils which contain many heavy hydrocarbons burn well on the reform burner, but unsatisfactorily on the Kosmos unless some lighter American oil has been added. If the problem is to find the most suitable lamp for a new kind of kerosene, Prössdorf (see above) advises that burning tests be made with the 28 different 14 mm.-models on the market, as well as on three 15 mm.-burners.

XIII. Calorific Value

According to O. Mohr, the different kerosene fractions from a specific gravity 0.793 to 0.812 and a flash point 22° to 37.5° have a heating value of 11,011 to 11,101 calories (see also page 57).

XIV. Source

Since it is sometimes useful to determine the source of a kerosene, several investigators have taken up this point (see also page 134 under the cold test of kerosene).

1. If a few drops of bromine are added to 2 to 3 c.c. of American kerosene, it decolorizes almost at once while almost all other oils remain colored for some time. An attempt * has been made to determine the source by means of the bromine and iodine values. The iodine value for solar oil was found to be 80, for Russian kerosene 0. to 1.6, American 5.5 to 16.5, Galician 0.1, Hanoverian 0.7.

The iodine value is influenced by the method of preparation of the

† Utz, Petrol., **2,** 43 (1906); Weger, same, 101; Graefe, Ztsch. für angew. Chem., **18,** 1580 (1905).

TABLE 34

German Railway Specifications for Kerosene in Force Beginning of 1913

State	External appearance	Specific gravity at 20° × 1000	Cold test	Flash test, Abel	Further points
Prussia, 1907	Clear, water-white appearance or slightly yellow; no odor of crude naphtha or crude oil	792–807 American, to 820 Russian, Austrian, Rumanian	....	Over 23°	Best refined, free from mechanical impurities, burning with clear, bright and white flame, neither smoking nor smelling. Specifications as to practical burning test will be given later
Bavaria, 1908	Clear, slightly yellow, faint odor	American not under 805, to 810 European	. .	American not under 24°, European not under 28°	Best refined, burning brightly, neither smoking nor smelling, no distillate under 100°; with European not more than 5 per cent over 300°, with American not more than 10 per cent. After 6 hours burning the wick should show at most only slightest incrustation, after 10 hours burning the candle power on a 12-mm. burner should show variation of at most 4 candle power
Saxony, 1903	....	....	American must be liquid at −15°, Russian at − 21°	Over 21°	Clean and burning without odor in proper lamps
Württem-berg, 1904	Clear, white to faint yellow, faint odor	To 800 American, to 830 Russian	.	American over 23°, Russian over 26°	Clean, free from acid; with sulphuric acid (50 c.c. of specific gravity 1.53 and 50 c.c. of oil) only a light yellow color should develop which should not get darker, the temperature should rise thereby not more than 2°; there should be no portion boiling under 90° and only very little boiling over 300°
Baden, 1910	Clear, faint odor	To 830 at 15°		Over 26°	Completely purified, free from acid, burning without soot or odor with a quiet flame which does not drop and which does not carbonize the wick, the incrustation on the wick not more than 0.1 gram for 1 kilogram, on standing should not change in color, combustibility, or candle power; naphthenic acids, etc., should be absent; on shaking with conc. sulphuric acid (sp. gr. 1.73) a color equivalent to 0.04 per cent of bismarck brown should develop
Imperial Territory, 1913	Clear	790–820	.	Over 23°	

kerosene (crack or steam distillation); in the cracking process unsaturated bodies with high iodine values are formed.*

TABLE 35

Origin of kerosene	Specific gravity	Iodine value (Waller)
American (Urania Salon)....	0.7915	7.0
American (Salon)	0.7909	6.8
American ...	0.7999	15.2
American (Kaiser)	0.7884	6.3
Russian (Meteor)	0.7997	3.1
Russian (Nobel)	0.8243	0.7
Galician (Reform)	0.8057	1.9
Galician.......	0.8096	0.7
	0.8092	0.9

2. The method proposed by Molinari and Fenaroli† for determining the origin of a kerosene by means of the precipitates caused by ozone is of more theoretical interest than practical value.

3. According to a method proposed by Arragon‡ the source of a kerosene was determined as follows: Equal parts of the burning oil and pure nitric acid (sp. gr. 1.4, freed from nitrous acid by boiling with urea) were shaken for a few moments. American oil gave a beautiful violet color, the acid becoming yellow; Austrian, Galician and Russian kerosenes became yellow, the acid, brown. By mixing the latter oils with American oil and acid, the entire mass became colored violet and after shaking for 10 to 15 seconds changed suddenly to yellow. In this way 10 per cent of Austrian oil could be detected when mixed with American. Graefe has shown by some experiments that several German oils also give a violet color.

D. Cleaning Oils

I. General

That portion of the petroleum distillates boiling between 100° and 150° and between 200° and 250°, which cannot be incorporated with the more valuable products, is used for cleaning plain or varnished metal parts. Variations from these limits occur; some of the lighter oils begin to boil at 70° like ordinary naphtha.

* Chemiker Zeitung, **37**, 2, 53, 86, 129, 158 (1913).
† Ber., **41**, 3704 (1908).
‡ Chem. Ztg., **33**, 20 (1909).

TABLE 36

German Railway Specifications for Cleaning Oils in Force Beginning of 1913

State	External appearance	Specific gravity at 20° ×1000	Cold test	Flash test O = open vessel, P=Pensky, A=Abel	Further requirements
Prussia, 1907	Clear, light colored, faint odor	800–850	. .	A over 30°	Free from acid, resin, fat and water and other impurities, must dissolve oil and loosen dirt particles easily, must not leave a greasy residue on the surfaces to be cleaned and must not attack varnish
Bavaria, 1912	Clear			P not under 70°	Should not attack paints or varnish, must not leave spots nor attack the eyes, ears or nose, should contain no mechanical impurities, should evaporate quickly, yet clean well and should not resinify
Saxony, 1913	Clear, light colored, faint, not unpleasant odor	800–850			Polished metal parts, varnish, paints and the hands of the laborers should not be attacked, consequently, no phenols or free acids should be present At least 90 per cent should distill between 200° and 250°
Württemberg, 1904	Clear, golden yellow		Still liquid at −2°	. . .	Must be free from coal-tar oils and water, must not attack paints and varnish, must leave no spots, and not attack the eyes, must not contain more than 1.5 per cent of insoluble components nor give a residue on distillation, all must distill over 130° and under 300°
Baden, 1910	Light yellow, translucent, no bad odor		Still liquid at −2°		Must be free from acids, resin, water, fat, fatty oils, and coal-tar oils, should leave no residue on distillation, 50 per cent should pass under 250° with none under 130° or over 300°, must not attack paint or varnish, should leave no spots, must not attack the eyes
Imperial Territory, 1912	Light yellow, faint odor	835–875 (15°)	Still liquid at −10°	O over 60°	Should be a refined distillation product of petroleum

II. Properties

Depending on the special requirements of certain trades and on the particular manner of use, various specifications as to inflammability, color and other properties are given. Paints, varnishes and metal must not be attacked; coal-tar oils should not be mixed with petroleum oils, as they are likely to attack the skin of workmen. See Table 36. See also lignite tar oils.

The differently boiling fractions also show differences in solubility; they may be miscible in all proportions with absolute alcohol, some may require at least two volumes of alcohol for solution, while those oils which resemble the lubricating oil fraction are only slightly soluble in alcohol. The flash point of the oils boiling over 200° (which are the most common) generally lies between 70° and 155° as determined in the Pensky apparatus (in a few instances at 38°), generally under 100°; the oils flash between 80° and 162° in an open vessel.

III. Tests

Adulteration with other oils is hardly to be expected on account of the cheapness of these materials, but if necessary the regular tests given under naphtha, lubricating oils, and general directions could be made. The properties are determined as with other mineral oils.

Test for Creosote: 100 c.c. of oil are shaken for 5 minutes in a graduated cylinder with 50 c c. of (sp gravity, 1.36) sodium hydroxide, and then allowed to settle for ½ hour (standing in hot water). The volume of the middle layer is determined when cold; one-half this volume is taken as the amount of creosote (Graefe). For a gravimetric determination, the total alkali layer is diluted with water, acidified with hydrochloric acid, extracted twice with ether, the ether then distilled, and the residue weighed. Prolonged drying may cause loss of creosote because of its considerable volatility.

For oils which contain several per cent of creosote the following method is suggested: The same procedure as just described is used with sodium hydroxide of specific gravity 1.16; two layers form, and from the decrease in volume, the per cent of creosote may be estimated.

E. Gas Oils

I. General

Gas oils are used for producing gas in retorts heated to a very high temperature, or for mixing with water gas in the process of carburetting, in which they are gasified in chambers heated to about 850°. They can be obtained not only from every crude oil but also from lignite tar

oils and from shale oil. As a matter of fact all mineral oils can be used for gas making, that is, changed to gas by dropping on hot surfaces, but naturally only those fractions are used which are not more valuable when used as illuminating or lubricating oils.

In the preparation of oil gas, the oil drops into a hot retort, decomposing into gas, tar and coke. From one kilogram of oil, 500 to 600 liters of gas, 300 to 400 grams of tar, and 40 to 60 grams of coke are obtained. In the water gas process, in the preliminary process, producer gas is formed, which, passing through the checker-work of the carburettor, heats this to a high temperature. If the gas oil is allowed to trickle into the carburettor while the water gas is forced in, there results a mixture of oil and water gas which has sufficient illuminating and fuel value to allow mixing with coal gas.

II. Properties

Gas oils, from petroleum, boil between 200° and 400°, that is between the boiling limits of illuminating and lubricating oils; gas oils from lignite tar are obtained on pressing the crude paraffin. Gas oils generally dissolve at ordinary temperatures in two volumes of absolute alcohol.

Since the introduction of incandescent mantles and the use of water gas in running stationary gas engines, the fuel value of a gas has become of greater importance than the illuminating power. A gas oil is, therefore, considered the more valuable the more it increases the heating value of the gas to be carburetted. Spiegel* proposes determining the value of gas oils from the amount of hydrogen contained, as found by elementary analysis. Ross and Leathes, however, found that this method is not free from fault† since the constitution of the oil is of influence on its carburetting value. Hempel‡ suggests using a so-called efficiency value, which is obtained as the product of the heating value and the amount of gas formed. If heated to within 40° of the suitable temperature (770°), the efficiency value remains constant, for although with change of temperature a decided difference in composition results, the energy relations remain unchanged.

* Jour. für Gasbeleuchtung, **50,** 45 (1907).

† Journal of Gaslighting, **1906,** 825.

‡ Jour. f. Gasbel., **53,** 53, 77, 101, 137, 155 (1910).

III. Tests

Specific gravity, boiling limits and flash point are determined as already described in other sections of the book; values thus obtained are used in determining the character of the oil. Sulphur in the oil does not make the oil useless for carburizing, for it will be almost completely removed in subsequent purification of the gas; an oil with 1 per cent of sulphur gave after gasifying only $\frac{1}{4}$ to $\frac{1}{3}$ gram of sulphur per cubic meter of gas.

Since adulteration is out of the question, the value of an oil is determined by the calorific value and the quantity of gas made. The gasifying power may be determined in larger experimental plants, or on a smaller laboratory scale.

(*a*) **Experimental Plant.** The installation of small gas plants, which involves considerable expense, is available only for the larger plants or establishments with considerable resources.

Description of a Practical Test Made with Mineral Oils at an Experimental Plant

The gasification was carried on in a bricked-in standard oil-gas furnace according to the exact directions of the consumer. The retorts were fitted with Le Chatelier thermo-couples. The stove and connections were brought to equilibrium in all parts by a preliminary test with lignite tar oil and during the gasifying process were washed out with the products of the test oil until equilibrium was certainly established and only the gas from the test oil was present. The amount of oil in general should be enough to supply a regular amount for 60 minutes; in this test it only lasted for 40 minutes. The amount of gas, the temperature and the rate of supply of oil were measured at 10-minute intervals. The progress of the test is given in the following data obtained by F. Frank with a normal gas oil.

Temperature of the upper retorts	Limits	670 to 690° C.
	Average	680°
Temperature of the lower retorts	Limits	740 to 750°
	Average	745°
Time of the experiment in minutes		40
Kilograms of oil gasified		12.91
Cubic meters of gas formed (metered)		7.70
Kilograms of tar (weighed in the separator)		4.45
Gas oil used per hour (kilograms)		19.37
Cubic meters of gas produced per hour		11.55
From 100 kilograms of oil were obtained cubic meters of gas		59.64
From 100 kilograms of oil were obtained kilograms of gas		34.47

The gas gave with a burner having a consumption of 35 liters per hour a Hefner candle power of 11.3 (average of 4 results measured at 10-minute intervals).

The oil corresponded, except for the tar formed, to the Prussian railway regulations existent at the time of test and the yield of gas and candle power was actually higher than specified.

Fig. 89 gives a diagram of an experimental gas plant used in Weban.*

(*b*) **Laboratory Examination.** 1. In order to determine the gasifying power of oils with the limited means of small laboratories, Wernecke

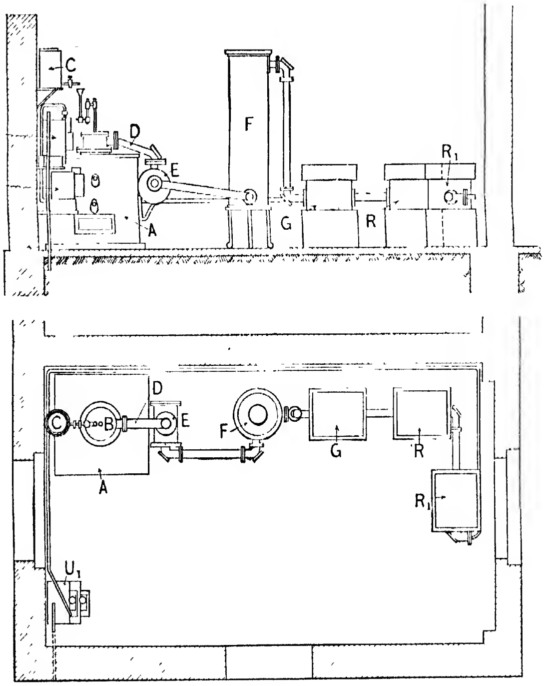


FIG. 89

constructed an apparatus in which the gas and tar from 100 c.c. of oil are determined. This apparatus has been tested and found useful. (Fig. 90.)

The oil to be tested is put into the Hoffman funnel and passes through the glass cylinder *i* and the U-tube *h* to the retort *g*. To determine the amount of oil gasified, the filling arrangement *sihk* is weighed before and after the experiment; the retort *g* and the tar separator oo_1 are also weighed before and after to determine the coke and tar formed. To allow a very slow delivery of oil to the hot retort walls, a needle valve is placed in *k*.

* Graefe, Laboratoriumsbuch, 160.

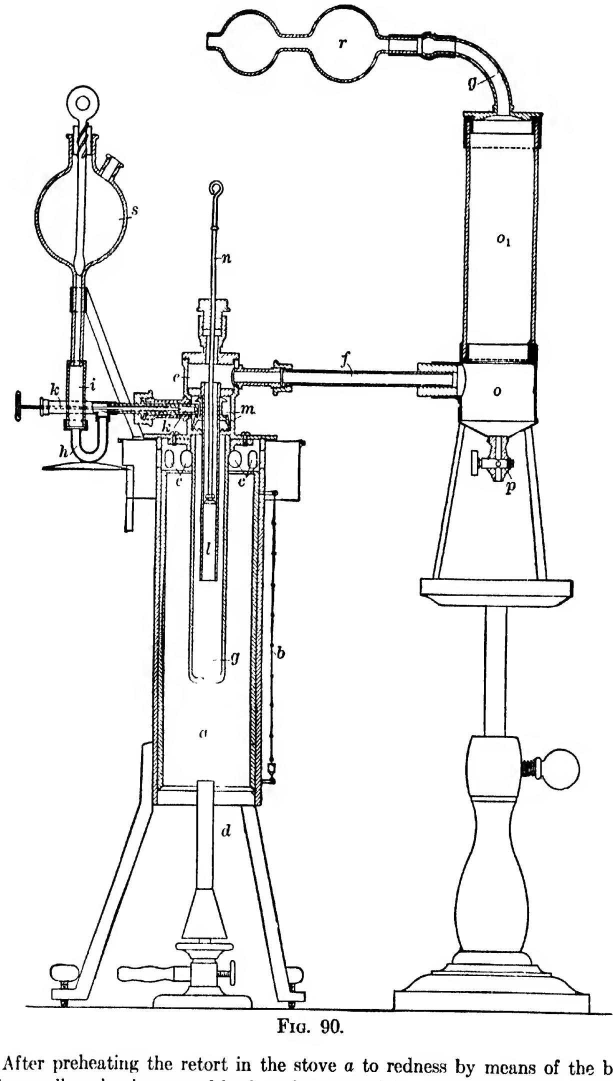


FIG. 90.

After preheating the retort in the stove a to redness by means of the burner d, the needle valve is screwed back as far as possible. The oil supply is regulated by turning the glass rod in the funnel so that the oil in the cylinder i always fluctuates near the zero point and so that 10 to 30 drops of oil gasify per minute; the oil is measured while the cylinder i is filling to the zero mark. During the process of gasifying, variations in the number of drops and the temperature are to be avoided.

The resulting gases and tar vapors pass through the tube *f* to the tar separator oo_1 and through *g* to the condensation pipe *r*. The gas passes to the gasometer where the amount is measured. Clogging of the tube *l* of the retort is made evident by the increase of pressure on the surface of the oil in the cylinder *i*; the clogging material is removed by the swab *n* without interrupting the test. The gasification may be considered normal when the escaping gas is brown and the tar is dark colored; white vapors and light brown tar point to incomplete heating.

2. **Apparatus of Ubbelohde and Philippide.** To avoid the faults of the Wernecke apparatus, variable temperature, insufficient heating, and at times overheating, Hempel constructed an apparatus* which however is difficult to handle. Ubbelohde† suggests the following (Fig. 91) as useful:

The seamless steel tube (1) (800 mm. long, 30 mm. diameter, 6 mm. thick) is heated electrically; the temperature is determined by a silver-nickel thermo-couple. The oil is pressed by hydrogen pressure (from 11) from the vessel (5) through a measuring device into the decomposing tube.

The tar produced is caught in the condenser (16) and collects in the receiver (13) from which it can be run through the cock (17). No tar collects in the emergency condenser (19). Gas passes through 3 wash bottles filled with mineral oil to catch benzine vapors, then to a gas meter, and finally to (24) for determination‡ of its density.

3. **Method of Ross and Leathes.**§ To have a simple means of determining the value of an oil, they gasify 15 c.c. from a retort (23 × 14.5 × 12 cm.) and determine the temperature with an electric pyrometer. The volume of gas formed and the amount absorbed by fuming sulphuric acid are determined. The product of the two quantities for Pennsylvania oil gasified at 760° is taken as a standard; the product for other oils compared with the standard as 100 gives the relative value.

TABLE 37

Kind of oil	Temperature of gasification	Volume of gas from one volume of oil	Per cent of heavy hydrocarbons	Relative value
Pennsylvania	760	529 9	30.1	100 00
Russian	680	465 7	34 2	99 86
Russian (refined)	680	429.0	31.8	85.53
Texas	610	325 0	30 1	61.25
Rumanian	760	459.7	28 6	82 43
Galician	680	452 8	35 5	100.78

* loc. cit.

† Philippide, Inaugural dissertation, Karlsruhe 1914; Chemiker Zeitung, **36,** 167 (1912).

‡ Hofsass, J. Gasbel **34,** 841 (1913); Z. angewandte Chemie, **27,** 137 (1914).

§ J. of gaslighting, **1906,** 825.

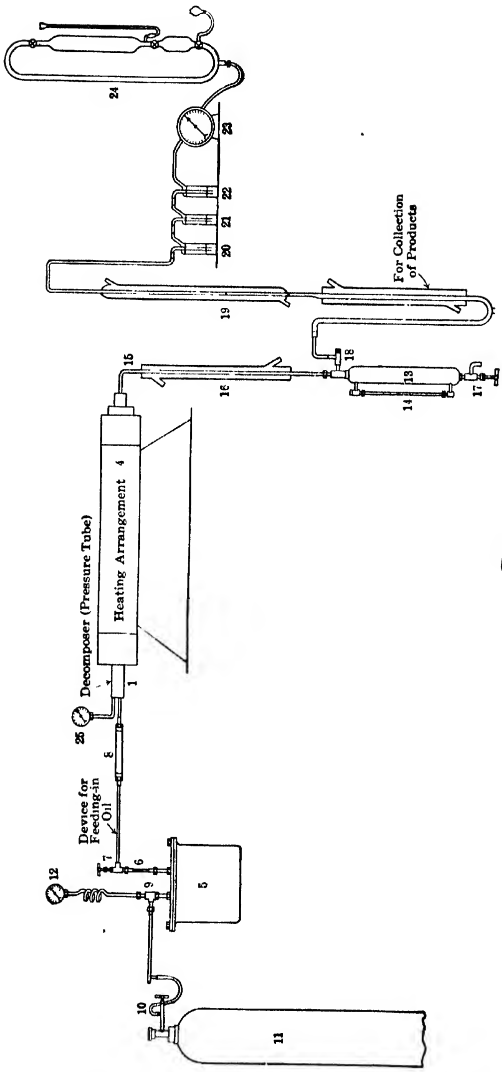


FIG. 91.

Experiments performed on a large scale showed that by this method the results are similar to carburizing in practice. By carburizing in the retort the part of the fuel value going into the gas is 5 to 10 per cent less than in the carburetor.

TABLE 38

GERMAN RAILWAY SPECIFICATIONS FOR GAS OILS IN FORCE BEGINNING OF 1913

State	External appearance	Specific gravity at 15° ×1000	Flash point *O* = open vessel, *P* = Pensky apparatus	Further requirements
Prussia, 1907	Clear, free from sediment	Up to 882 (20°)	. ...	Lignite tar oil, clear, transparent, free from water and sediment. 100 kilograms should yield at least 54 cubic meters of gas at the rate of 10 per hour, which gas with a consumption of 35 liters per hour should give 11 candle power, small residue when gasified, less than 2 per cent of creosote, no oils (so-called "dead oils") which have been freed of creosote. A fuel value will probably be required
Bavaria, 1907	Clear, yellow, faint odor	850–900	*O* not under 85° *P* not under 70°	Not more than 2 per cent of creosote, paraffin in traces, sulphur content of the gas prepared not more than 0 35 gram per cubic meter. 100 kilograms of oil should give at least 50 cubic meters of pure gas, which should with a consumption of 35 liters per hour give 11 candle power
Saxony, 1903	....	....	... .	Dark lignite tar oil (paraffin oil) should not be so viscous at 15° that it clogs the tubes leading to the retorts. 100 kilograms should give at least 50 liters of gas of 11 candle power
Württem-berg, 1904	Yellowish brown, faint odor	860–890	....	100 kilograms of oil should give at least 56 cubic meters of gas and 44–50 per cent of tar; at least 11 candle power with a consumption of 35 liters per hour, not more than 2 per cent of creosote
Imperial Territory, 1912	Clear light brown, transparent	850–875	Over 45°	Free from tar and water, at least 500 liters gas from 1 kilogram, not more than 2 per cent of creosote, with an hourly consumption of 35 liters and at 8 mm. water pressure at least 10 candle power
Royal Powder Works, Spandau, 1911	Light yellow, clear, no rancid odor	Over 850	....	Doubly refined, well-filtered paraffin oil, less than 2 per cent of creosote, unmixed with other oils, with narrow boiling limits, nearly all boiling under 300°, Engler viscosity at 20° under 3

(The specifications of Baden only require that the oil be tested in the apparatus of Wernecke.)

F. Transformer Oils

I. General

The transformers of electric power stations are often immersed in covered vessels filled with mineral oil to prevent heating or short circuiting; these oil reservoirs often have a capacity of several cubic meters. The oil is used because of its insulating power and low dielectric constant. Air is said to have* a dielectric resistance of 4000 volts, mineral oil about 9000 volts, and rosin oils of about 20,000 volts.

II. Requirements

The oil† used for transformers must be carefully freed from water and mineral acids so that it will be a good insulator and will not attack the copper or the insulation. It must also be non-volatile since it is heated to 90° in the transformers and considerable surface is exposed for evaporation. On heating for several hours to 100°, it should show no decomposition nor should any precipitate collect on the cold surfaces; such separated asphaltic portions interfere with the operation of the transformer since they cling to the windings and prevent the carrying off of the heat through the oil. Cotton threads hung in the oil must show no decrease in strength due to acidity produced by the heating of the oil. The oils should remain liquid at − 20°, since some transformers are placed in the open and are exposed to severe cold in winter.

III. Properties

Light-colored, mobile mineral lubricating oils, when highly refined, meet the conditions demanded of good transformer oils.

A mineral oil of absolute viscosity 0.69 ($E = 10$), after heating five hours at 100° in the apparatus of Holde (see page 182), lost only 0.06 per cent; after heating two hours at 170° it had lost only 1 per cent. The mobile lignite tar oils evaporate much more at 100°; they appear to be unsuited for the purpose. Mineral oils in general tend to decompose on continued heating, with oxidation and separation of asphaltic and resinous products (see page 187); if an oil decomposes it soon shows a cloudiness and later a flocculent yellowish to brownish precipitate of oxidation products; it also becomes asphaltic on heating and is no longer completely soluble in naphtha.

* Pumphrey, Oesterr. Z. Elektrotechn., **1906**, 58.

† Holde, Mitteilungen, **22**, 147 (1904); Brauen, Chem. Umsch., **21**, 138, 170 (1914).

For these reasons Brauen gives the heavy, thrice refined rosin oils the preference; because of their ring-structure (terpene derivatives) they decompose less easily than the mineral oils with open chains. The acidic materials formed on heating in a transformer are soluble in the rosin oil, and are less acidic and attack metals less than decomposition products of mineral oils, which also happen to be insoluble and interfere with the insulating power. Rosin oils thicken more easily than mineral oils (after heating five hours at 100° they show from 1 to 1.5 per cent loss by evaporation; after two hours at 170° they had lost from 5.6 to 7.4 per cent) but as the viscosity of rosin oils decreases with temperature rise more rapidly than the viscosity of mineral oils, the thickened rosin oil at the temperature of the transformer will still be mobile enough to allow circulation, and conduction and convection of heat.

IV. Specifications for Switch Oils

Oil is also used for oil switches to prevent arcing of high-tension currents. For this purpose oils free from water and acid must be used; they should also be resistant to cold and have a high flash and burning point. The oil should be mobile, in order that it may quickly penetrate the broken circuit and extinguish the arc.

Rosin oils are much carbonized by the arc, because of their high carbon content, whereby they lose in their insulating power. Mobile mineral oils with the following properties should be used for this purpose: Flash point (open dish) over 170°, burning point over 200° C., specific gravity 0.880 to 0.900, viscosity (Engler) at 20° under 10, cold test under − 20°.

V. Testing of Transformer Oils

Formerly the heat capacity of transformer oils was determined (for different viscous oils, this lies between 0.40 and 0.50) but this is unnecessary, since it is less a question of heat capacity than of the dielectric strength of the oil at the temperature attained during maximum load. The dielectric strength and the rise of temperature during load are both dependent on the viscosity of the oil, the heat capacity playing only a minor part.

1. The insulating power is determined according to page 64 by measurement of the conductance. If the insulating power is unsatisfactory the oil is rejected for use as a transformer oil. A value for the specific resistance greater than 10^{-13}, by the Siemens method, is not considered satisfactory.

2. Resistance to discharge is determined if the oil is otherwise satisfactory.

The testing of the oil* is carried out in a 200 c.c. vessel, 3 cm. in diameter, filled with oil, in which a spark gap is placed and the voltage at which sparking begins measured. The depth of immersion of the spark gap must always be the same; the balls must be well polished. The presence of water, of air bubbles and of small threads have a decided effect on the result.

Another method consists† in determining the voltage at which a continuous discharge takes place between two steel balls of 10 mm. diameter placed vertically 5 mm. apart. The oil is heated to 80°, and then with decreasing temperature, the voltage determined at which a continuous discharge passes through the 5 mm. thick layer of oil (see Table 39).

TABLE 39

Temperature	Voltage
68	50,000
59	48,000
45	45,000
34	43,000
26	40,000

Experiments on the relation between the viscosity of the oil and the resistance to the discharge were carried out by Breth.‡ The more mobile oils have the higher resistance. Since in using mineral oils a separation of asphalt takes place, greater with heavy oils than with light, the mobile oils are to be preferred for this reason also.

The following specifications for transformer and switch oils have been suggested by the German electrical manufacturers:

1. Only clean refined mineral oils should be used (rosin oils should not be mixed with mineral oils. Testing see page 198).

2. The specific gravity should lie between 0.85 and 0.92 at 15°.

3. The Engler viscosity should not be more than 8 at 20°.

4. The flash and burning points, determined in an open dish by the method of Marcusson, should not be under 160° and 180° respectively.

* Elektr. Anzeiger through Organ f.d. Oel- und Fett-handel, Nr. 54, **1904.**

† Chem. Rev., **16,** 232 (1909).

‡ Petrol., **7,** 290 (1911).

5. The freezing point should not be above $-20°$. In a test tube 15 mm. wide in a layer 4 cm. deep, after cooling 1 hour to $-20°$, the oil must still be liquid when inverted, and clear.

6. The loss on heating to 100° for five hours must not be over 0.4 per cent.

7. The oil should be free from acid, alkali, sulphur and absolutely free from moisture.

8. The oil should be clean; suspended particles, threads, sand, etc., must be absent (determined by pouring through a sieve of 0.3 mm. mesh).

9. After passing a stream of oxygen for 70 hours through the oil heated to 120°, the oil must still be clear and completely soluble in naphtha (0.700). The tar value should not be greater than 0.1 per cent. See page 188.

The following tests are also useful:

Testing for free alkali: The oil is dissolved in a neutralized mixture of alcohol-ether (1:4) and if a red color develops in the presence of phenolphthalein, the free alkali is titrated back with $N/10$ hydrochloric acid.

Resinification test. In carrying out test number 9 (above) 150 grams of sample are heated in a 400 c.c. Erlenmeyer flask for 70 hours at 120°, bubbling through the oil a stream of oxygen (using a tube at least 3 mm. wide) at the rate of 2 bubbles per second. To test for tarry matter after the above test is finished, 50 grams of oil are heated in a flask under a reflux for 20 minutes with a solution of 1000 parts by weight of alcohol, 1000 parts of water and 75 parts of sodium hydroxide. After detaching the condenser the warm mixture is shaken 5 minutes, put into a separatory funnel and as much as possible of the alcoholic alkali filtered off. 40 c.c. of the filtrate are acidified with hydrochloric acid and the tarry matter is dissolved in benzol; the extraction with benzol is repeated. The benzol solution is washed with water and then evaporated in a glass dish. The residue is dried for 5 minutes at 100° and weighed.

G. Motor and Fuel Oils

I. Motor Oils

For internal combustion motors and Diesel motors mineral oils are used as the source of power. The use of gasoline as an automobile fuel has already been considered on page 115. As fuel for the Diesel motors* can be used not only crude oil distillates, such as kerosene, gas oils, solar oil, lignite tar oils rich in paraffin, but even crude oils themselves are available, since the resinous and high boiling part is completely burnt by the hot compressed air in the explosion cylinder.

* Rieppel, Z. Ver.d. Ing., **1907**, 613; Kutzbach, ibid., **1907**, 521; Constam and Schläffer, ibid., **1913**, 1489; Holm, Zeit. angew. Chem., **26**, 273 (1913).

Diesel motor fuels may be divided into three classes: 1. Those of general applicability, containing more than 10 per cent of hydrogen, such as crude oil from which the naphtha has been distilled (calorific value over 10,000 calories) and lignite ta. oils (9700 calories). 2. Oils of limited usefulness as they require motors of special construction, such as coal tar oils (calorific value not less than 8800 calories, coke residue not more than 3 per cent), and certain tars (water-gas, oil gas, retort oven tars, with not more than 3 per cent of water, fuel value over 8600 calories). 3. Material in general not usable but combustible under certain conditions (horizontal and inclined retort tars).

The heat of combustion at constant volume, as determined in a bomb, cannot be used. From it must be subtracted the external work done in evaporating the water formed during combustion. The heat of reaction of the fuel at constant pressure must be calculated from heat of reaction in the bomb. See pages 49 and 55. The heat of combustion at constant pressure for kerosene is about 10,600 calories, for petroleum gas oils and lignite tar oils about 9,800, and for coal tar oils about 8,900 calories.

Mechanical impurities must be avoided. But the asphalt content of the oils does not affect its usefulness, for residues of asphaltic oils have been successfully used in Diesel motors.

A content of sulphur has no effect on its fuel value, but an oil low in sulphur is preferred because it does not attack the exhaust pipes. A harmful action of the products of combustion on the parts of the motor need not be feared. So long as water remains uncondensed, corrosive action is retarded; the corrosive action will, therefore, be confined to the exhaust, since the water remains in the form of vapor in the motor.

Since the motors are in general constructed for a certain kind of fuel-oil, the laboratory examination will be concerned with comparing the oil with previously used material and establishing its origin by means of the general tests already described.

The following specifications* have been suggested for motor oils.

The oil should be liquid at 0° as otherwise too much heat is necessary to get it into usable condition. Ten grams of the oil, shaken with 10 c.c. of xylol and filtered, should not give more than 0.04 grams residue on the paper. The coke residue should not be over 3 per cent since otherwise asphaltic oils will give a coke-like residue in the cylinders. Free carbon causes stoppage of valves and deposits on the cylinder walls and should therefore be present only in traces. At least 80 per cent should distill below 350°. The Abel-Pensky flash point should lie between 60° and 100°.

* J. C. Allen, Heavy Oil as Fuel for Internal Combustion Engines, Washington (1913). Petroleum, **10,** 16 (1914).

The calorific value should be over 9000 calories. Not less than 10 per cent of hydrogen should be contained. Sulphur not over 0.75 per cent. Free acid and alkali should be absent. Not more than 0.05 per cent of ash, not over 1 per cent of water is allowable, as each per cent of water lowers the fuel value 1.06 per cent. Creosote up to 12 per cent may be present, even if it may cause smoke. Paraffin must not be present to more than 15 per cent as it requires more oxygen for combustion and causes disturbances in operation.

TABLE 40

SPECIFICATIONS FOR DIESEL MOTOR OILS (IN FORCE BEGINNING 1913)

State	External appearance	Specific gravity at 15° C.	Flash point, O = open, P = Pensky	Further Requirements
Bavaria, 1908 .	....	0.830 to 0 900	P not under 70°	Creosote not over 2 per cent; fuel value at least 9500 calories.
Imperial Territory, 1912	....	0.830 to 0.880	O not under 80°	Crude-oil distillate, free from water, burning in Diesel motor without residue, fuel value at least 10,000 calories.

II. FUEL OILS

Crude petroleum, its liquid distillation residues, and tar oils are used as fuel* in locomotives, steamships, oil refineries, and manufacturing establishments. Oil has, as a fuel, greater calorific value than coal, is handled and transported more easily, occupies smaller storage room, burns with less smoke, soot and dust evolution, is controlled more easily and requires less attention for regulating the combustion.

The examination may be restricted to a determination of the calorific value (page 49). For identification the usual determinations, specific gravity, flash point, viscosity, etc., are made. At times the behavior on cooling is observed (pages 34), since easily solidified oils may cause trouble in the supply pipes and the orifices of the burners. Sulphur may be determined during the course of the combustion in the bomb (page 54). Sand and ash are estimated by the methods described on pages 73 and 74.

* Zaloziecki — Lidow, Naphtha 1904, No. 21, 22.

The United States Bureau of Mines* has given the following requirements for a fuel oil. Most important is the calorific value which should be at least 10,000 calories. The flash point should not be under 60°; all low-boiling oils must have been removed by distillation. The specific gravity should be between 0.85 and 0.96 at 15°. The oil must remain liquid at 0° and not contain more than 2 per cent of water and 1 per cent of sulphur.

TABLE 41

CALORIFIC VALUES AND ELEMENTARY ANALYSES OF VARIOUS FUELS†

Material	Specific gravity at 15°	Per cent			Fuel value, calories	Heat of combustion referred to liquid water
		C	H	O		
Paraffin oil (from brown-coal tar)	0.915	85.42	11 33	3 25	9,790	10,440
The same	0 890	85 58	11 49	2 93	9,836	10,454
Solar oil (from brown-coal tar). . . .	0 825	85 48	12 31	2 21	9,988	10,653
Kerosene	0 796	84 76	14 09	1 15	10,305	11,066
Same	0.789	85 24	14 34	0 42	10,335	11,109
Naphtha. . .	0 716	85 20	14 80		10,359	11,157

The values given for oxygen in the case of the brown-coal tar oils include sulphur also.

H. Oils for the Laying of Dust

The use of oils to lay the dust on streets depends on the very slow evaporation of the heavier components, on the ease of oxidation to asphaltic bodies and on the disinfecting action of the tar and tar oils. The tar applied hot is brushed into the street, or an emulsion of oil and water is used. The materials best suited for the laying of dust are crude oils, heavy asphaltic oils, oil residues, tars, liquid asphalts, or a mixture of tar and clay.

In printing establishments and type foundries, the floors are oiled regularly, since after one treatment with non-drying oil they can be swept without raising the dust. In some respects this is not satisfac-

* Petrol., **7**, 153 (1911).

† Langbein, Ztschr. f. angew. Chem., **13**, 1266 (1900).

tory, because the floors become slippery and are thus likely to lead to injury.

A series of floor oils was examined by R. Heise* who showed that water-soluble oils (which before use are diluted with water) are not desirable. Of the oils insoluble in water, the less viscous pure mineral oils are the best. Among the insoluble oils examined were found pure mineral oils with color and perfumes added, and mixtures of mineral oil with fatty oils (linseed, colza oil, lanolin) containing also color, perfumes and disinfectants.

Addition of perfumes is not desirable, addition of nitrobenzol is dangerous; the addition of fatty oil leads to stickiness and dirty floors. Krist† claims that several per cent of olein may be added to the oil with advantage as the washing of floors with soapy water or dilute alkali is made easier. To decrease the " bloom " of mineral oils quinoline yellow may be used but nitronaphthalin should not be used (see page 75) as it darkens in sunlight and therefore colors the floors a dark color.

For oiling wood floors pure mineral oil should be used to prevent rancidity, and to avoid slipperiness an oil of specific viscosity 30 to 40 at 20° is advisable. The oil should not get sticky after several weeks.

To determine the tendency to gum 1 c.c. of oil is spread over a glass dish and exposed to the air and light for 4 weeks; at the end of this period it should be easily removed without leaving a tough film clinging to the bottom of the dish.

Krist thinks that floor oils should be pure mineral oils of not too high viscosity so that they may readily penetrate the pores of the wood, and conversely easily rise by capillarity to the dust layer and bind it. The oil should be odorless, of specific gravity 0.80 to 0.88 and Engler degree not over 6.5 at 20° C. He considers mineral oils as unsuited for oiling linoleum floors.

J. Lubricating Oils

I. Refining

The source of lubricating oil is petroleum from which the lighter components (naphtha and kerosene) have been removed by distillation; the residue thus obtained may be used directly as a lubricant, or used after refining with sulphuric acid, or separated by distillation with superheated steam into various fractions and other residues. By

* Arbeiten aus dem Kaiserlichen Gesundheitsamt, **30**, Heft 1 (1909).

† Leifensiederztg., **40**, 850, 879 (1913).

mixing some of these fractions with others, or with distillation residues a variety of products may be obtained with a variety of properties (viscosity, flash point, specific gravity). This is the principle on which the industry is based. The separate fractions are further refined to remove odor, resinous materials, as well as to attain the desired lightness of color. This is accomplished by means of sulphuric acid, agitating with a stream of air, the acid being later removed by washing with alkali or water. The purification may also be brought about by filtration through fuller's earth (customary in the United States).

In Europe the oil is distilled with superheated steam, recently also with partial vacuum, direct firing being avoided, to avoid decomposition. Commercially the distillates are separated according to specific gravity, flash point and viscosity.

In the United States direct firing is much used in separating the crude oil fractions, thus increasing the yield of naphtha and illuminating oils. The refining, however, is carried on with superheated steam.

Certain grades of crude petroleum, after dehydration and separation of sand and mechanically admixed material, and after distilling the more volatile components, may be used directly for lubrication.

II. General Considerations

A lubricant should prevent direct contact between the bearings and the moving parts of machinery, avoiding friction and wear, thus substituting for metallic friction the much smaller internal friction of the lubricant. The more completely this problem is solved under the conditions of temperature, speed and pressure, the more valuable the lubricant from a mechanical point of view. Whether the mechanically most efficient lubricant is the most economical depends somewhat on the ratio of efficiency, the amount used and the price of the material; greases have a low mechanical efficiency compared with the liquid oils but from the point of economy and cleanliness they are far superior.

Only liquids with great tendency to adhere* to solids are suited for lubrication since only these have the property to penetrate by capillarity where journal and bearing are the closest and where the danger of contact and wear is the greatest. The lubricating oils prevent direct contact of the metal surfaces because of their adhesion to these surfaces and because their viscosity keeps them from being squeezed out by the pressure on the bearing.

Experience has shown that the power to adhere to metals increases with the viscosity of the oil. Since the danger that an oil will be pressed

* Ubbelohde, Petrol., 7, 773, 882, 938 (1912).

out increases with the pressure on the bearings, it is advisable for high pressures to use oils of considerable viscosity. According to Petroff* the total frictional resistance of lubricated surfaces is proportional to the internal friction (viscosity) of the oil and to the speed of the moving parts but inversely proportional to the pressure. With low pressure and high speed there should be used a very mobile oil, with higher pressure and great velocity more viscous oils. If, for example, a spindle rotating with practically no pressure but very rapidly were lubricated with a very viscous oil, it would mean a lavish waste of power. On the other hand, with high pressures as in transmission gears, to avoid loss and waste of oil, a grease would be the logical lubricant to apply.

According to Ubbelohde and contrary to earlier assumptions, the external friction (the friction between the liquid and the bearing) can be neglected. Only the internal friction viscosity is of importance in lubrication. Although the viscosity of the fatty oils varies only within narrow limits, the mineral oils from which most of the lubricating oils are nowadays made show degrees of viscosity ranging from that of spindle oils as mobile as kerosene to that of dense heavy cylinder oils. The peculiar composition (mixtures of high boiling hydrocarbons) of the mineral lubricating oils determines two unchangeable properties of such oils: a slight volatility (with corresponding constancy of volume and slight fire-risk) and a certain viscosity (which the lighter petroleum distillates, naphtha, kerosene, do not possess) which allows the formation of a layer between the metal surfaces to which it clings tenaciously.

The practical man is interested in knowing how much the use of a certain lubricant will cut down power losses. It is unfortunately true that this question cannot be answered directly from a consideration of either the viscosity or the behavior with a mechanical testing machine. While the viscosity of oils is probably most important in determining the lubricating power, other factors are undoubtedly concerned. Fatty oils and mineral oils of the same viscosity do not have the same power to retain a lubricating film; the fatty oils are said to adhere more firmly to the bearing. Surface tension may play a part in this; other hydrodynamic properties may be concerned. This can only be shown by further experimentation. But certainly the variation of the viscosity with the temperature is an important consideration; an oil may be of proper viscosity at low temperature but be unsuited to the conditions of use at a higher temperature.

In selecting a mineral oil or other lubricant, besides considering the pressure, velocity and viscosity factors, some thought should be given

* Theorie der Reibung. Hamburg and Leipzig, 1887.

to the temperatures to which it will be subjected under service. The lubricant and bearings of railway rolling stock may be cooled in winter to as much as twenty degrees below zero; if oils, like rape, or mineral oils containing much paraffin, were used for such service, one might expect them to solidify and cause an enormous loss of power. This is confirmed by actual experience, so that now the railway specifications call for oils still liquid at $-20°$ C.

In refrigerating machinery even lower temperatures may be reached; in the liquefaction of gases temperatures as low as $-100°$ C. must be expected. In the latter case naphtha or graphite may be used as the lubricant.

In the steam cylinders of certain engines temperatures as high as 300° may be attained; in the explosion cylinders of internal combustion engines, in spite of air or water cooling, even higher temperatures are reached. More moderate temperature changes take place in ordinary machinary bearings; as a result of the friction between the metal surfaces, heat develops and warms both oil and bearings.

Lubricating oils should show only slight volatility at the temperatures attained in service; like all liquids, lubricating oils are volatile much below their boiling point. Fatty oils volatilize with decomposition only on strong heating (to 300°). With mineral oils, by evaporation of the more volatile components, the consistency changes, and with hot bearings, the volume may decidedly decrease. The air in the work rooms is also contaminated by the too great volatility. Moreover, because of the fire-risk, only non-volatile oils with a high flash point should be used. Steam cylinder oils must be particularly non-volatile because of the high temperature of the superheated steam (300°), the highest boiling fractions of petroleum, vaseline-like products, being used for this purpose.

The oil should not lose its power of reducing friction by evaporation, by gumming or by acting chemically on the metal of the bearing or journal. Bone oil, sperm oil and olive oil in thin layers show only slight changes in their properties, while rape oil under the same conditions becomes gummy. Mineral oils free from asphalt are not affected in thin layers when exposed to the air but oils containing asphalt cause an increase in friction and produce deposits in the cylinders. The lubricant should not contain drying oils or rosin oils, nor even traces of mineral acids (from the refining). For cheaper lubricants small amounts of organic acids do not interfere with their practical use. With steam turbine oils, not only must there be no acid present when purchased, but long continued action of air and high temperature must

not produce acidic products in the oil; soaps may form and slimy emulsions may be produced under unfavorable circumstances. For this reason it is desirable, here as with transformer oils, to determine the tendency to resinify which is a measure of the tendency of the oil to form organic acids under the influence of air and high temperature.

Mineral oils, if not thickened, or if nearly free from asphalt or mechanical impurities, are soluble in naphtha, benzol, carbon disulphide, chlorinated hydrocarbons or ether. They are not suited for certain kinds of airplane motors (Gnome) which are lubricated by blowing in the gasoline and lubricant together; for this purpose castor oil which is insoluble in naphtha has been used.

Obviously, the use made of the lubricant determines the properties specified since no one lubricating material is applicable to all cases. Various companies (railroad, steamship) have accordingly issued specifications for oils suitable for their purposes.

The fatty oils generally used are raw and refined rape oil, mustard oil, olive oil, castor oil, neat's-foot oil, bone oil, sperm oil, tallow, palm oil, wool fat and blubber oils. Raw rape oil mixed with dark mineral oils is now little used in the lubrication of locomotive cylinders; in place of these mixtures, there is used almost pure mineral oil containing very little tallow or bone oil.

For reasons of economy and of cleanliness, as well as for certain uses for which oils are not applicable, greases are used. Greases find application with heavily loaded bearings, especially when exposed to a temperature as high as that of the rolls in steel rolling mills. They must be well mixed and should not melt under 80°; some melt as high as 200°. They contain, besides mineral oil, sodium, calcium, or magnesium soaps, and water. Mixtures of wool fat, tallow, alkali soaps, with mineral oils are found on the market, also greases containing graphite, which are used for cogwheels and for bicycle chain lubrication. On standing or in use they should not separate into layers and should not undergo oxidation in service, nor evaporate. The value of a grease depends on the quality of the added oil, the proportions of oil, soap and water, and the absence of loading materials (talc, barytes, starch). Wagon grease may contain besides the oil, soap and water, less valuable materials such as rosin oil, brown-coal tar oils, loading materials and often the more viscous of the residues obtained in mineral oil distillation.

Mineral oils containing graphite or salts of naphthenic acids are used as conducting lubricants for sliding contacts. Mineral oils mixed with thickened fatty oils (rape) are used for marine engines. For the

driving mechanism of torpedoes fatty oil mixed with mobile mineral oil is used as the lubricant. For clocks and other chronometers mixtures containing neat's foot oil are used.

This does not exhaust the list of lubricating materials. In the preparation of liquid oxygen an aqueous solution of glycerine is used, since oils in contact with the compressed oxygen would be instantly burned. In preparing liquid chlorine, since the chlorine attacks organic lubricants, concentrated sulphuric acid is used as the lubricant. In refrigerating machinery using sulphur dioxide, liquid sulphur dioxide itself is used as the lubricant. Glycerine lubrication has been found satisfactory in compression machinery for carbon dioxide. In liquid air machines, very low boiling naphthas are used.

With boring, cutting and shaping machines, liquids are used primarily for cooling the metal surfaces; these are not lubricants in the ordinary sense. Ordinary water cannot be used since it rusts the surfaces exposed. Formerly soapy water was used; in the last ten years a so-called water-soluble mineral oil has been tried. The oil is suspended in alkali soaps.

For hardening steel, animal fats (tallow) have been found useful, though mineral oils have been used when fat was not available. For preventing corrosion of metal parts of machinery, it has been customary to cover them with oil or grease. The oils used must not be too mobile. Vaseline, wool-fat and similar materials have been used. In foundries mineral oils have been used as binding materials in the foundry sand instead of the expensive linseed oil. Mineral lubricating oils are also added to olein or olive oil for use in the textile industry. Because of the insulating power of lubricating oils they are used as transformer and switch oils.

III. Lubricating Devices

The great variety in the form and use of machinery brings with it a multiplicity of lubricating devices,* the object of which is to lead the lubricant to the bearing surface in a manner which is automatic, economical and able to keep the oil free from dust. There are different types of oil-feeders: those which supply oil continuously, those which act only when the movable part is in motion and those which function with the assistance of pumps. To the first group belong the many forms of wick, dropping and needle oilers which are placed over the

* Rudeloff, Ver. d. Ing., **33**, 1047; L. Singer, Ueber die Schmierung von Maschinenteilen, Petrol., **7**, 1307 (1912); Engler-Höfer, IV, 619.

shafting; these also supply more oil during movement because of suction. The second class includes the pad, spiral and ring lubricators in which the oil reservoir is beneath the journal. The third form is used in steam-cylinder lubrication as well as with turbines, recently also in machine shops. For details on the construction see the machinery handbooks.

Physical Tests

IV. External Appearance

The color, degree of transparency, odor and consistency give the skilled observer valuable hints for estimating the worth of a lubricant and for choosing the best method of investigating it. These properties are observed in a test tube 15 mm. wide.

(*a*) The color has no influence on the lubricating power; it is used only in identifying the sample. The color may range from water white to yellow, yellow red, blood red. Unless treated with substances like nitro-naphthalene, American oils fluoresce with a grass green color, Russian with a blue sheen, which is particularly evident when a drop is placed on a sheet of black glazed paper; mineral oils containing anti-fluorescents, and fatty oils, appear jet black in this test. Oils containing distillation residues or not filtered through fuller's earth (such as some railway oils) are brown to green black in reflected light. Probably all machinery oils are distilled and, therefore, transparent in a test tube.

(*b*) The following are the different degrees of consistency as determined by external appearance (for a determination of viscosity see page 7): quite mobile like kerosene, small viscosity like spindle oils, medium viscosity like light machinery oils, quite viscous like heavy machinery oils, very viscous like liquid cylinder oils, like salve (thin or thick) like lard, like butter, like tallow.

With steam-cylinder oils, movements and temperature changes before testing often cause a decided change in the viscosity. To get an accurate determination of consistency, the oils are put in a 15 mm. test tube, heated 10 minutes in boiling water and then kept one hour without movement in a water bath at 20°. The consistency is then tested by inclination of the test tube. Oils containing rubber make it evident by their peculiar behavior; they show a tendency to stringiness on dripping from a glass rod, or between the fingers (see page 202). The addition of soaps may cause similar phenomena; if, after decomposition of these in ether solution with hydrochloric acid, the stringiness persists, the presence of rubber may be considered probable.

(*c*) By rubbing some of the oil on the hand, or by gentle heating, the characteristic odor of the oil may be detected. A glue-like odor may be attributed to bone or neat's-foot oil; the odor of rape oil and of mustard oil is also very characteristic. Rosin oil and coal-tar oils can also be detected by the odor. If, however, nitrobenzol is added, or if the oil has been properly treated with steam or with chemical reagents, these odors may be so reduced that even large amounts can no longer be thus detected.

(*d*) Cloudiness may be due to solid particles. If the oil is spread in a thin film over a glass plate, solid particles, which melt on heating, are often visible. These may in some cases be due to the addition of thickening material to mobile oils. The cloudiness due to the presence of solid hydrocarbons will disappear on warming to 40 to 50° and then gradually return on cooling.

Turbidity may also be due to small amounts of water contained. The cloudiness disappears on warming; small visible drops of water will appear at the bottom, or cling to the sides of the test tube. If the oil is heated until foaming ceases, the turbidity will not return. Oils containing water will foam and bump on heating.

(*e*) Mechanical impurities, such as straw particles, which are easily recognizable in clear and light colored oils, may be collected even in dark oils by passing about 250 c.c. of oil through a sieve of 1/3 mm. mesh. For quantitative determination see page 73.

V. Specific Gravity

For the methods and significance of this constant see page 2. For lubrication, other things being equal, oils of low specific gravity are preferred, as this gives for a given weight of oil a larger volume of lubricating material.

According to Mendelejeff the following corrections for high-boiling Russian petroleum products are to be applied:

Specific gravity	Correction for 1° temperature difference	Specific gravity	Correction for 1° temperature difference
0 860–0 865	0 000 700	0 890–0 895	0 000 650
0 865–0 870	0 000 692	0 895–0 900	0 000 640
0 870–0 875	0 000 685	0 900–0 905	0 000 630
0 875–0 880	0 000 677	0 905–0 910	0 000 620
0 880–0 885	0 000 670	0 910–0 920	0 000 600
0.885–0 890	0 000 660		

VI. Coefficient of Expansion

The determination of this quantity has already been considered on page 5.

(*a*) The values for α for heavy viscous mineral machine oils (sp. gr. at least 0.908) between 20° and 78° range from 0.00070 to 0.00072. With oils containing suspended solid vaseline or pitch particles the value of α between 12° and 20° is somewhat higher (0.00075 to 0.00081) than for homogeneous oils because of the melting of the solid particles.

With mobile oils (used for oiling easy running parts, spindles, small dynamos, etc.), with specific gravity less than 0.905 the value of α is greater than with the heavy machine oils (0.00072 to 0.00076 between 20° and 78°).

With homogeneous liquid mineral oils α increases with the temperature similar to the behavior of all homogeneous liquids; with oils containing suspended solid particles it first decreases till all solid is melted, then it increases. Paraffin on melting expands more than the liquid, therefore the specific gravity and the fluidity of the solutions of paraffin in other oils are lower than for the original oil. Dissolving 1 to 1.5 per cent of paraffin in a paraffin-free Russian oil lowers the fluidity 10 to 15 per cent, the specific gravity from 0.0001 to 0.003.

The value of α is different with oils of different source but of the same viscosity, corresponding to the difference in their chemical composition. The change of α mentioned allows the easy recognition of paraffin and pitch particles.

In Fig. 92 are given graphs of the change of the coefficient of expansion with the temperature of various typical mineral machine oils; in Tables 43 and 44 are given the coefficients of expansion of American cylinder and machine oils, together with other properties.

(*b*) The correction for the change of specific gravity from a given temperature to a higher or lower one is in general the product of the coefficient of expansion and the specific gravity; for liquid mineral lubricating oils for each degree this is 0.00063 to 0.00072 or about 0.00068 on the average.

The correction* for the specific gravity of vaseline-like very viscous cylinder oils for which α lies between 0.000777 and 0.000876 is to be taken as 0.00075 on the average. In some cases lower values were found. For Rumanian crude oil residues, according to Singer, α lies between 0.00073 and 0.00079.

* Mitteilungen, Ergänzungsheft V, 23 (1895).

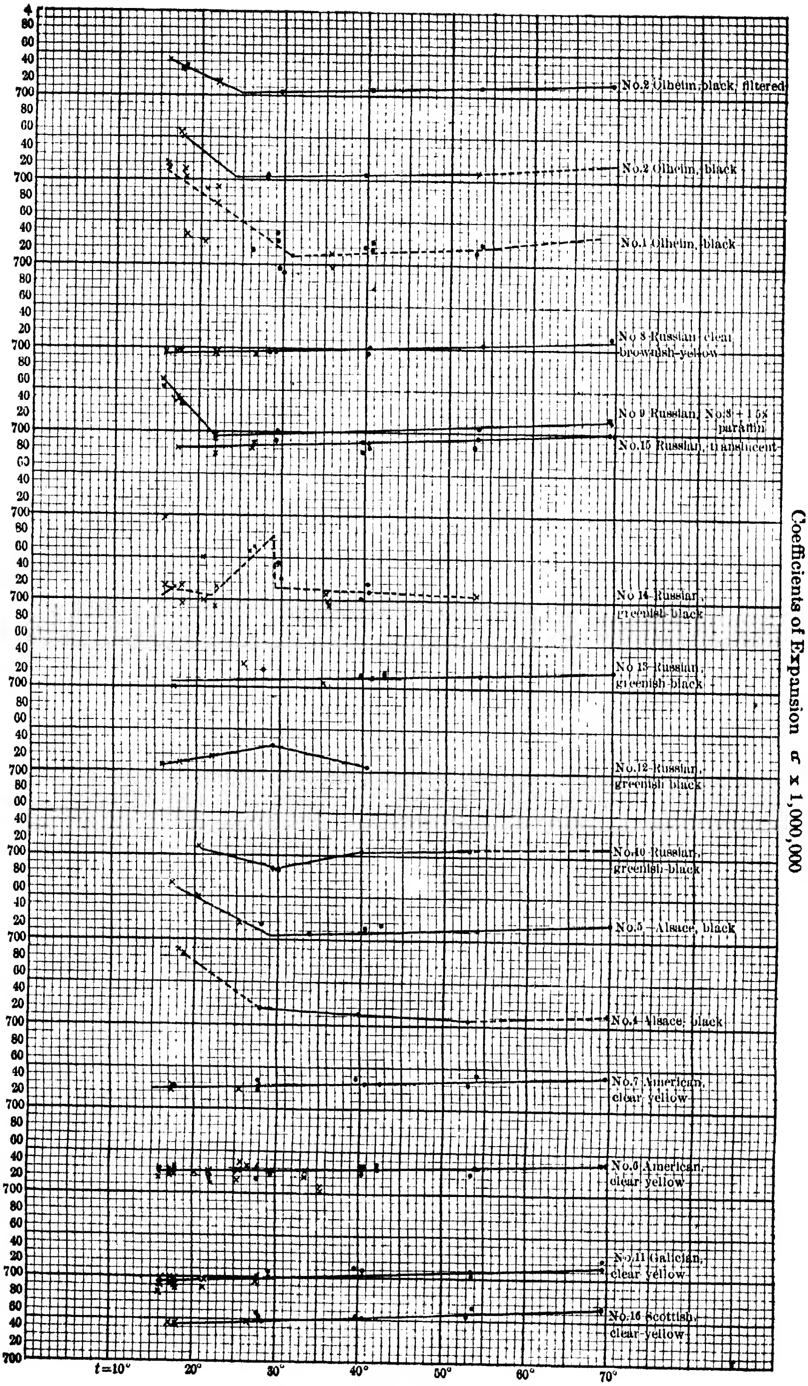

No.3 Olheim, black, filtered
No.2 Olheim, black
No.1 Olheim, black
No 8 Russian, clear brownish-yellow
No 9 Russian, No.8 + 15% paraffin
No.15 Russian, translucent
No 14 Russian, greenish-black
No 13 Russian, greenish-black
No.12 Russian, greenish black
No.10 Russian, greenish-black
No.5 Alsace, black
No.4 Alsace, black
No.7 American, clear yellow
No.6 American, clear yellow
No.11 Galician, clear yellow
No.16 Scottish, clear yellow
Coefficients of Expansion α x 1,000,000
t=10°
20°
30°
40°
50°
60°
70°

FIG. 92.

TABLE 43
AMERICAN CYLINDER OILS

Color	Specific gravity at 15° × 10,000	Engler viscosity at		Solidification point in test tube		Flash point, Pensky-Martens, °C	(α) (10⁸) between °C.		
		100°	180°	°C.	Consistency		20-35	35-61	61-78
Dark green, opaque	8946	2 97	1 32	+25	thick, salvelike	232	869	755	730
Green black opaque	9078	3 90	1 40			270	896	734	709
Dark green, opaque	9028	3 91	1 36	0	thick, salvelike	267	829	788	710
The same	9030	3 91		0	thin, salvelike	270	846	712	696
Dark green, opaque.	9029	4 27	1 40			269	806	700	710
Brown black, opaque	9166	6 00	1 51			278	781	702	683
Black, opaque	9165	6 40	1 53			293	670	711	694

TABLE 44
AMERICAN MACHINERY OILS

Color	Specific gravity at 15° × 10,000	Engler viscosity at		Flash point, Pensky-Martens, °C	(α) (10⁸) between °C		
		20°	50°		20-35	35 61	61-78
Greenish yellow, clear.	8994	9 5	2 70	201	726	732	740
Green, brown red, clear	8932	19 2	4 35	197	741	733	736
Green, brown red, translucent.. .. .	8834	25 1	5 50	186	726	738	757

VII. VISCOSITY

As already stated on pages 7 and 167, the viscosity is the most important dynamical constant for lubricating oils which can be easily determined in the laboratory. And for fresh fatty oils, not thickened by polymerization, or oxidation, or both, it is a criterion of purity (see Tables 95 to 98, page 422 and following). Practical experience has shown what viscosity values should be specified for certain uses (page 212), temperature, pressure, and velocity being the factors to be considered.

The following is a classification* of oils according to Engler degrees and flash point (Pensky-Martens).

Spindle oils (with E 3.5 at 50° and 5 to 15 at 20°; flash point 140 to 200° C.) are used for machines with small pressure and high velocity. For separators, centrifuges, turbines, light transmission, rapidly moving steam engines up to 20 H.P., electric motors, dynamos, bicycles, sewing machines, high speed presses, automobiles, compressor oils.

Light machinery oils (with E 3.5 to 5.5 at 50°, and 25 at 20°: flash point 170 to 220°) may be substituted for rape and olive oils for transmission, for all purposes where heavy spindle oils are used, for ventilators, threshing machines, and steam engines with not too high bearing pressure.

Heavy machine oils (with E 5.5 at 50°, to 60 or higher at 20°; flash point, 190 to 220°) are used as cylinder oils if E is greater than 3 at 100°. In heavy machines, transmission.

Factors for converting Engler degrees to specific viscosity or absolute viscosity have already been discussed on pages 15, 23, and 27. At present, specifications are usually stated in Engler degrees but it is to be hoped that the viscosity values may be used in the future.

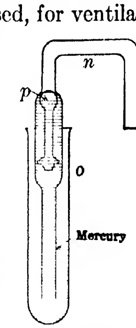


FIG. 93.

Laboratory methods have already been described on page 16. In using the method of Holde the pictured safety valve (Fig. 93) will be found useful. Industrially the Engler apparatus with open oil-bath is still used instead of one with a closed water bath. The oil-bath allows overheating of the jet; this form of apparatus should therefore be rejected. The temperature regulation at 100° with the oil bath is much more difficult than with a water bath.

VIII. Mechanical Testing

The mechanical testing of oils is carried out in practice on simple specially designed machines with experimental journals and bearings approximating the conditions of service, with thermometers attached for measuring the temperature of the bearings and some arrangements for measuring the power consumed, the latter giving a measure of the friction in the lubricated bearings. The machines described in the literature give directly or indirectly the frictional coefficients, that is, the frictional resistance reduced to unit pressure and unit velocity.

* Singer in Engler-Höfer, Bd., IV, 634.

The frictional coefficient depends on the pressure, on the velocity of the rotating shaft, on the metal of the journal and bearing, and upon other factors. The difference in the radius of the bearing and of the journal is of great influence on the coefficient of friction.

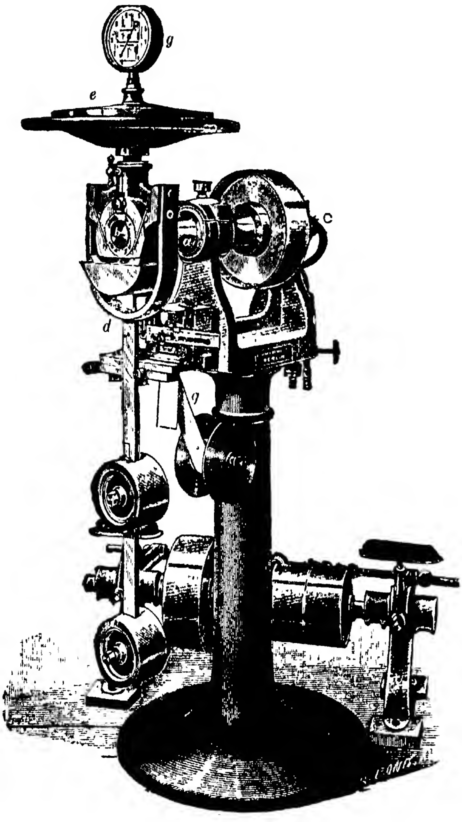


Fig. 94.

The different oil-testing machines differ considerably from each other as well as from the actual working machines, consequently the frictional coefficients are not comparable with each other, nor are they capable of being directly transferred to practice; they are valid only for the particular conditions of the machine tested. In many cases, as for the lubrication of steam and gas motor cylinders, of steam turbines, etc., the conditions of use of the oil are not even approximated. It does however permit a study of the effect of certain additions to the oil (such as graphite, rubber, etc.) on the coefficient of friction.

In choosing oils for purposes where the conditions of use cannot be exactly defined but only approximately characterized, there are used typical oils which have been satisfactory in practice; or various oils are directly tested in the machine in question, and the consumption and other points of comparison recorded. In the first case the ordinary chemical and physical tests are sufficient to characterize the oil.

The Martens machine* is in principle the same as that of Thurston and in the Kgl. Materialprüfungsamt is used for testing oils with the common horizontal position of the journal, under varying conditions of speed, pressure and temperature. (Fig. 94.)

It consists of a shaft *a* and an experimental journal *b* which are given velocities of 0.5 or 1.0 or 2.0 meters per second; the journal carries a pendulum *de* with an instrument recording the deviation of the pendulum. The lubrication is effected by the bath *f*; the bearing and oil can be heated or cooled by circulating water or steam. The journal and shaft are hollow and provided with a spraying arrangement for heating and cooling, for regulating the temperature of the film of oil. The journal, 100 mm. in diameter and 70 mm. long, is made of steel and must be perfectly round and highly polished. The machine is run with rouge and oil till, after a series of experiments, the pendulum always swings to the same position.

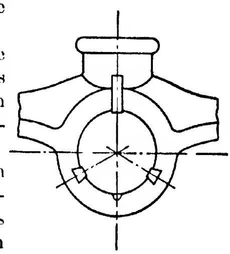


FIG. 94a

The coefficient of friction is determined, from the swing of the pendulum and the pressure of the bearings against the journal, by the Napoli compressor *e* which is screwed into the head of the pendulum. The pressure is shown by the manometer *g*.

To get a perfectly uniform pressure the brasses which are used do not completely surround the journal but, instead, three bronze bearings are placed 120° apart (as shown in Fig. 94a), fastened in the cast iron pendulum in such a way that a layer of oil of about 0.5 mm. thickness will separate the journal and the body of the pendulum. Sometimes bearings which are semicircular are used. The thermometer is bent at right angles. The swing of the pendulum indicates the friction or indirectly the coefficient of friction.

The following are the conditions of use in the Materialprüfungsamt (pressure and temperature):

TABLE 45

With $p = \frac{Q}{3f} =$	10	25	40	53	66	80	93	106	119	132	145	158	*at*
And 0 5 meter per sec ..	22 0	22 8	23 5	24 1	25 4	27 0	29 4	33 0	38 5	45 0	52 0	....	....
And 1 0 meter per sec .. .	23 5	26 8	30 0	33 2	36 8	40 7	45 0	49 5	55 0	61 4	68 0	....	°C.
And 2 0 meters per sec	31 0	34 5	38 0	41 7	45 3	48 6	54 5	59 5	65 5	72 0	79 0	....	....

where *Q* is the total load in kilograms and *f* the active surface of one bearing expressed in square centimeters. When the correct temperature is attained the machine is run for 5 minutes longer; the pendulum may change its position somewhat under these conditions but this may be neglected.

The machine is controlled now and then by using fresh refined rape oil or a refined mineral lubricating oil. The coefficient of friction must come out within an

* To be obtained from the Deutschen Waffen and Munitionsfabrik in Karlsruhe. Described Mitteilungen, 8, 1 (1890); also Engineering, July, 1894.

error of 10 per cent under similar conditions of experiment; if this is not the case, the machine must be run under an average pressure of 50 to 70 kg until the normal condition is reestablished; this sometimes requires several weeks.

Many other machines have been suggested but cannot be described here. Among these might be mentioned that of Dettmar,* manufactured by Lahmeyer & Co., of Frankfurt a.M., that of Fein-Kapff,† the machine of Kirsch of Vienna, the apparatus of Wilkins‡ and the Ossag machine of the Stern Oil Works of Sonneborn.

IX. Behavior on Cooling

For a general discussion of the determination of the solidification limits of oils see page 34. The following method for the numerical comparison of the fluidity of cooled mineral oils is used by the Prussian railways (Fig. 95) and the Materialprufungsamt (Figs. 96 to 98).

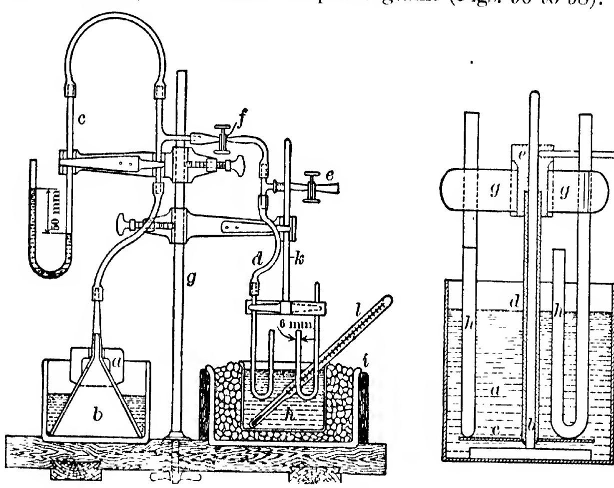


FIG. 95.

1. The well-mixed sample is poured through a 1/3 mm. meshed sieve to separate gross impurities. To determine the effect of heating on the cold test, two unheated samples, and two samples, heated for 10 minutes in a water bath kept at 50° and then kept for 30 minutes at + 20°, are compared. Special tubes are used (Fig. 97).

2. The oils are put in the U-tubes by means of a pipette (Fig. 96); on the shorter arm is found a millimeter scale, graduated upwards from 0. The width of the tubes

* Ding. Poly. Jour., **1900,** 88.

† Ding. Poly. Jour, **1900,** 608; Ver. Deutsch. Ing., **1901, 343.**

‡ Elektrotechn. Zeitschr., **1904,** Heft 7.

should not vary more than 0.3 mm. from 6 mm. in the bend and should be measured beforehand with small steel balls, 5.7 and 6.3 mm. in diameter; the smaller should pass through the tubes, the larger should not.

3. (Fig. 98.) A funnel, weighted with *c*, closed at the top by the water manometer and the pinch-cock *k*, is put into the vessel *b* containing water. A pressure which is measured on the manometer is thus developed in the funnel. To obtain exactly 50 mm. pressure, water is poured into *b* or the cock *k* is opened, *l* being also open.

4. The samples are cooled for one hour. Then the long arms of the U-tubes in the freezing mixture are connected with the manometer by rubber tubing, the

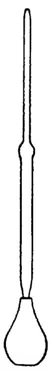


FIG. 96

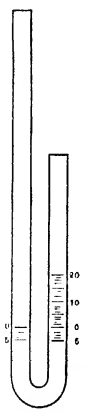


FIG. 97.

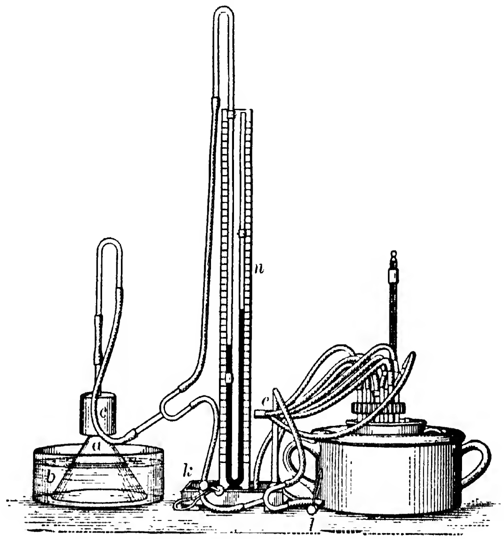


FIG. 98.

pinch-cock *l* having been previously removed to avoid compression when slipping on the tubes. The pressure is exerted on the oils for one minute, *l* having been slipped on and *k* being open; by then quickly removing *l*, the ordinary pressure is obtained. The rise in the column of the short arm, which can be recognized by the wet surface when the oil flows back, is taken as a measure of the fluidity of the oil. Any turbidity or separation of paraffin is simultaneously observed.

X. VOLATILITY AND FLASH POINT

The mineral lubricating oils should volatilize only on strong heating. The flash point was formerly considered as the only means of estimating the volatility of the oils, open or closed testers being used according to the object of the examination. The quality of machine oils, especially of steam cylinder oils, is often judged by the height of

the flash point; this can, however, give only an approximate idea of the volatility of a lubricating oil. With a noteworthy low flash point a distillation should be made in an Engler flask to determine the presence of kerosene or naphtha fractions or in the absence of any of these, a direct evaporation test can be made. Such a direct test should be made only in the case of steam cylinder oils, steam turbine or transformer oils.

Besides the flash point, the burning point or fire test is used to more definitely characterize its volatility; it is the temperature at which the oil will continue to burn on its surface if a test flame is brought near. This test is considered by some to be a better test of the volatility of lubricating oils than the flash point, because the latter, especially in the closed tester, shows the presence of only traces of easily inflammable vapors (naphtha).

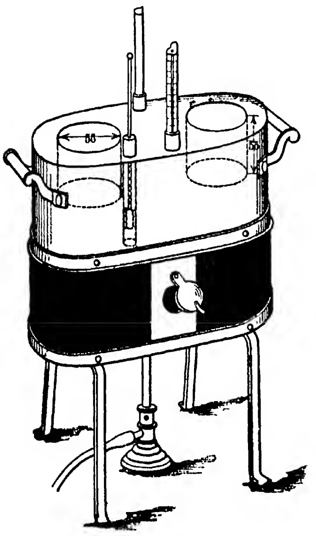


FIG. 99.

(*a*) **Volatility.** For this the arrangement of Holde* may be used. The apparatus consists (Fig. 99) of an external heating bath in which a vessel similar to the oil container of the Pensky apparatus is placed (as a substitute may be used a similarly proportioned porcelain dish since it is lighter and more easily weighed and is said to prevent the oil from creeping over the side). The heating bath, according to the temperature desired, may be filled with liquids of proper boiling point; this temperature should be somewhat higher than that of the oil itself since the inner cup never reaches the temperature of the outside bath.

A gas heater may be used surrounded by a safety wire gauze, thus avoiding danger of igniting the oil; the burner is ignited through the opening in front (Fig. 99). Instead of a gas burner, an electric heating arrangement may be obtained. In the gas burner, the burner itself passes through a small hole in the bottom.

In the small vessel is placed some glycerine (for tests up to 200°) or high boiling cylinder oil with flash point above 300° (for temperatures up to 300°) in order to transfer the heat from the outside bath to the Pensky oil container. The oil is placed in the latter up to the mark (3.5 cm. high).

A thermometer is dipped into the inside cup to determine the temperature of the oil sample; after each removal from the oil it must be wiped with weighed filter

* To be obtained from Paul Altmann, Berlin, N. W., Luisenstr. 21.

paper so that none is lost; this must later be weighed with the oil and Pensky cup. After heating the required length of time, cooling and drying in a desiccator, the cup is reweighed.

For determinations over 300° up to 350° C. the oil is heated in the Pensky flash point apparatus with a triple burner; this requires, however, constant attention.

By this method after two hours heating to 200° of steam cylinder oils of flash point 250 to 300° a loss of 0.03 to 0.10 per cent took place; two hours at 300° gave a loss of 0.2 to 1.2 per cent; at 350°, 8 to 15 per cent was lost. The apparatus gives results which can be checked on repetition. It is used (by the Prussian railways) in testing steam and cylinder oils.

(*b*) 1. Another method for determining volatility consists in heating 10 grams of oil in glass dishes (85 mm. diameter and 20 mm. high); these dishes are heated in double-walled drying ovens. The results do not agree with those of the Holde method as the conditions of experiment are different.

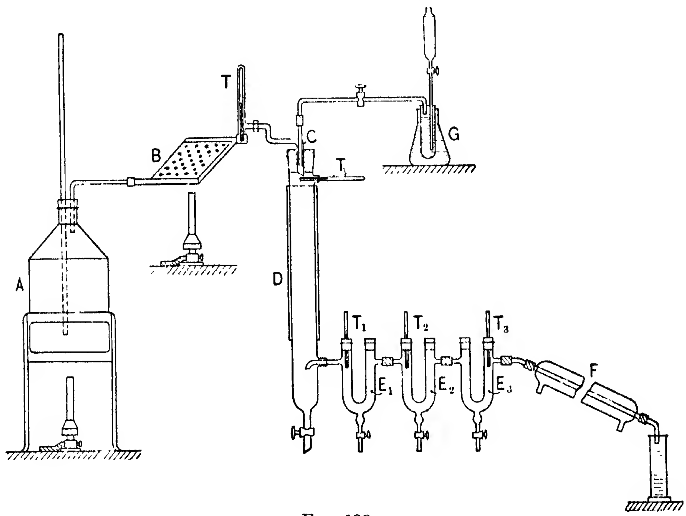


Fig. 100.

2. Camerman and Nicolas,* by passing steam superheated to 300° into a cylindrical vessel, conical at the bottom, into which at the same time the oil to be tested is dropping, determine how much oil evaporates in a given time and how much is not carried away. The part remaining is the useful portion; the more non-volatile matter present in the oil, the more valuable it is considered.

* Mitteil. d. Intern. Verb. f. d. Materialprufungen d. Technik, 1910, Heft. 15, 186.

This method has been improved by Kammerer, (Fig. 100) as follows:

The steam generated in (A) is superheated in (B) to 300°. The temperature is read at T where the steam passes into the asbestos-covered vessels (D), the oil being forced from (G) into (C) by mercury pressure. Oil and steam are mixed by a sieve (a). The oil carried over is caught in (E_1), (E_2), (E_3) and is condensed by (F). In 1 hour one kilogram of water and 10 c.c. of oil evaporate. The oil not condensed in E_3 at the temperature T_3 is caught after passing (F) and amounts to from 2 to 30 per cent according to the oil and temperature used.

For flash point determination, see page 38.

XI. Optical Properties

See page 57 and following. Mineral lubricating oils have at 18° refractive indices ranging from 1.4755 to 1.517, heavy rosin oils from 1.530 to 1.550; so that an adulteration of the former by the latter may be recognized by means of the refractive index, if the amount of the rosin oil added is not too small.

Plane polarized light is rotated by mineral oil from 0 to 1.2 degrees (rarely as much as + 3.1°) while rosin oils show a rotation from + 30 to + 50 degrees.

Chemical Tests

XII. Free Acid and Free Alkali

In pale refined mineral oils usually no free acid is found or at most only traces exist (to 0.2 per cent, calculated as oleic acid). In dark oils, the acid content may rise to 2 per cent (in rare instances, to 3.5). As a rule, however, the acid value of dark oils is not more than 1 per cent. Oils containing less than 0.07 per cent are considered as free from acid. See page 69 for the method of determination.

The presence of free alkali is shown by the red color of phenolphthalein in a benzol-alcohol solution of a pale oil, or an alcoholic extract of a dark oil. The amount is determined by titration with $\frac{N}{10}$ hydrochloric acid.

XIII. Resin Content

(*a*) **The Natural Resins of Mineral Lubricating Oils.** Resinous bodies are found in unadulterated mineral oils in a colloidal condition as may be seen in the ultramicroscope.* They may be classed as those sol-

* Holde, Ztchr. f. Chem. u. Ind. d. Colloide, **1908**, 274; Zeit. f. angew. Chem., **21**, 6 (1908).

uble and those insoluble in 70 per cent alcohol. The alcohol-insoluble materials are those black asphalt- and pitch-like bodies found in all dark oils (see page 104). The content of alcohol-soluble resins in light-colored oils is generally not more than 0.6 per cent; in dark oils not more than 1 per cent; in poorly refined oils it may be 3.5 per cent. All the resins are soluble in benzol and the solutions leave on evaporation varnish-like residues, more or less solid. The light-colored resins are sometimes completely, sometimes only partially, soluble, in petroleum ether. In alcohol-ether (4:3) and (3:4), the resins, soluble in 70 per cent alcohol, dissolve completely. The characteristic reaction for colophony (red-violet coloration of the solution in 1 c.c. of acetic anhydride on the addition of a drop of sulphuric acid of sp. gr. 1.530) is not given by these resins. Some of these resins show a neutral character.

According to Holde and Eickmann* all pale and dark lubricating oils, contain, apart from the asphaltic and pitch-like bodies of dark oils, from 2 to 3 per cent of resins which are adsorbed by bone-black. These resins have a specific gravity of more than 1, oxygen content 3 to 6 per cent, 1 to 2 per cent of sulphur, iodine number of 13 to 26, and are soluble in benzol or chloroform but not in naphtha; when dissolved in the oil, they are also soluble in naphtha.

It may be presumed that these resins were formed in the mineral oils by the condensation or polymerization of unsaturated bodies with an addition of sulphur or oxygen or both.

Marcusson† later isolated these resins in greater quantity by allowing the oil dissolved (1:8) in naphtha to be absorbed by fuller's earth and then extracting with low boiling naphtha in a Soxhlet apparatus; by then extracting with chloroform, he obtained solid, red-brown to brown-black resins which melted on a water bath.

Schwarz‡ claims that the resinifying components of steam turbine oils are present in the acetone-soluble portion and amount to from 10 to 30 per cent. A Russian machine oil had a tar value of 0.76, the (19 per cent) acetone extract a value 1.8 while the (81 per cent) acetone insoluble portion showed only 0.55; the coke values were 0.28, 1.7 and 0 respectively. By shaking a naphtha solution of the acetone extract with castor oil the resins were concentrated still more. The portion soluble in castor oil (25 per cent of the acetone extract, equivalent to

* Mitteilungen, **25,** 148 (1907).

† Chemiker Zeitung, **39,** 581 (1915); Zeit. angewandte Chem., **29,** 349 (1916); Mitteilungen, **34,** 374 (1916).

‡ Zeit. angewandte Chem., **26,** 385 (1913).

4.5 per cent the orginal oil) showed, on separation of the castor oil by saponification, etc., different constants:

	Density	E_{50}	Index of refraction	Iodine value
Extract	1 0152	37.6	1.578	12.4
Original oil .	9085	6 7	1 498	6.0

(*b*) **Detection of Rosin (Colophony).** The resins are rarely added to mineral oils as adulterants. The test for colophony will, however, be given since it will be necessary to refer to it later.

1. **Qualitative.** Colophony would be revealed in mineral lubricating oils by a high acidity. An acid value of 14 (corresponding to 7 per cent of oleic acid) is equivalent to 9 per cent of colophony which consists principally of abietic acid* (American rosin) or the isomeric pimaric acid (French rosin). Colophony, according to the quantities of other components present, has an acid value of 140 to 170.

The qualitative test for rosin (which is unnecessary if the oil is free from acid) is made by shaking 8 to 10 c.c. of oil with an equal volume of 70 per cent alcohol; after cooling, the solution is run through a filter moistened with 70 per cent alcohol and the filtrate evaporated. In the presence of colophony the residue will have a resinous, but not oily, consistency. It is dissolved cold, by rubbing with a glass rod, in some acetic anhydride and then a drop of sulphuric acid of specific gravity 1.53 added. A violet color is obtained; this must be looked for at once since, on standing, the color changes to a neutral brown (Morawski reaction). The residue will react with alcoholic sodium hydroxide with the formation of rosin soap.

2. **Quantitatively** the determination of rosin is effected in the absence of oil or fatty acid by extraction with caustic soda solution and by then weighing the acids precipitated from the alkaline extract with mineral acid.

5 to 10 grams of oil are dissolved in 50 c.c. of ether and then shaken with 50 c.c. of KOH solution (10 grams KOH, 10 grams alcohol, 100 c.c. water); the ether solution is washed repeatedly with water, twice with 10 c.c. portions of KOH solution and again with water, till the latter remains colorless. The united aqueous-alkaline extracts are then shaken with 50 c.c. of ether to separate mechanically adhering

* Abietic acid $C_{20}H_{30}O_2$ can be obtained pure according to P. Levy, D.R.P. 221,889 of 1908, by adding to a cooled alcoholic solution of the rosin an alcoholic solution of sodium ethylate thus precipitating the sodium salt in white needles, which are dried by suction and dissolved in water. By adding mineral acid the free abietic acid is precipitated and then purified by recrystallization from methyl alcohol or glacial acetic acid.

oil particles, the ether shaken with 5 c.c. of alkali, and then this alkali added to the rest of the alkaline extracts. The solution is acidified with HCl, then shaken with 50 c.c. of ether, and the ether washed with water till free from mineral acid; the ether is then evaporated and the residue weighed; multiplied by 1.07, it gives the resin content.

In the presence of fatty acids proceed according to page 471.

XIV. Gumming and Oxidation Tests (Thin and Thick Films)

(*a*) **Tendency to Resinify.** Stringent specifications regarding stability during the lubrication are especially necessary with steam turbine oils which are heated for a long time to high temperatures.* With former methods of lubrication new oil was constantly replacing the used or lost oil; but with the more modern ring-oilers and other devices, the same oil comes again and again in contact with the bearing, and therefore the oil should remain unchanged for a long time.

Distilled mineral oils (light and dark) do not become resinous on standing for months at 50° or at 100°. After 35 hours at 100° practically all machine oils will evaporate if spread out in thin films. Dark oils containing considerable quantities of residues resinify to some extent after standing for a long time at room temperature and at higher temperatures (50 to 100°) there is a decided thickening, the more volatile hydrocarbons escaping to a large extent. Some oxidation and some polymerization also take place, the pitch and asphaltic bodies being concentrated in the residue. For example dark oils after 35 hours heating in a thin layer became gummy and dried up, while at 50°, corresponding more to actual use, they became only more viscous but not gummy; rape oil under the same conditions dried up almost entirely. The tendency to become resinous is made less by treatment of these oils with naphtha or alcohol-ether which removes the heavy pitchy and asphaltic materials. The determination of pitch and asphalt in dark oils, especially in the case of steam-cylinder oils, is considered helpful since these are exposed to high temperatures. (See page 106.)

To carry out the resinification test, which in general can be omitted with mineral oils, one drop of oil is spread on a glass plate (5 × 10 cm.) (machine oils are heated to 50°, steam-cylinder oils to 100°) and daily observations are taken of the consistency of the oil layer on cooling.

* Couradson [Chem. Ztg., **36**, 1220 (1912)] states that the precipitates formed during the use of steam turbine oils are metal soaps formed by the combined action of air, water and several metals on the oils; the presence of one metal alone causes almost no change in the oil, so that it seems as if an electric difference in potential is the cause of the formation of acid and soap.

Spread in a thick film (0.2 to 0.25 gram of oil on a plate 75 sq. cm. area) light lubricating oil distillates show no tendency to become resinous at 100° while high-boiling colored distillates containing 1 to 3 per cent of resinous material will become gummy on heating for 9 to 15 months at 100°. Dark oils containing residues give with the above test after a few months gummy residues, after 15 months solid resinous or pitchy deposits.

The resins remaining after heating the mineral oils are insoluble or only slightly soluble in naphtha; in benzol they are completely soluble.

(*b*) **Kissling's Resinification Constants.** Formerly in the lubrication of bearings a constant stream of fresh oil replaced that used up or dropped off; in the newer lubricating devices the same oil is repeatedly brought in contact with the bearing, so that there must now be much more stringent requirements regarding the stability of the oils, especially with steam turbines, where the oils are subjected to high temperatures for a considerable time. For the purpose of testing the changeability of oils, Kissling* has proposed four new tests which are designed to determine their stability. These give the tar value, coke value, tar-forming value and coke-forming value. By heating the oil with alcoholic sodium hydroxide and then acidifying, a certain amount of tar, which can be extracted with benzol, is obtained; this is known as the tar value. By determining the amount of material insoluble in petroleum ether after separating the tarry substances, the coke value is obtained. Kissling therefore proposes to examine oils in regard to their tendency to give this tar value and coke value before and after heating to a high temperature, the difference in the respective values being called tar-forming or coke-forming value respectively.

1. **Tar Value.** 50 grams of the lubricating oil are warmed in a flask with air condenser to about 80° with 50 c.c. of alcoholic sodium hydroxide (50 grams alcohol and 50 grams of a 7.5 per cent solution of NaOH in water) and then shaken vigorously and continuously for 5 minutes. The mixture is put into a separatory funnel, allowed to separate hot, and then after cooling, as large a part as possible of the alkaline solution containing the tarry matter filtered; the clear solution thus obtained is acidified in a separatory funnel and extracted with two 50 c.c. portions of benzol. The benzol is evaporated, the residue weighed and the weight thus obtained, calculated to 100 grams, gives the tar value.

2. **Coke Value.** The oil freed from tar by shaking with sodium hydroxide is treated with 500 c.c. of petroleum ether of which 90 per cent must distill between 30° and 80°. Allowed to stand over night and then filtered, the separated coke

* Chem. Zeit., **30,** 932 (1906); **31,** 328 (1907); **32,** 938 (1908); **33,** 521 (1909); Chem. Umschau, **13,** 302 (1906); **16,** 3 (1909); Petroleum, **3,** 108, 938 (1907).

particles are caught on a filter paper, dried at 105° to constant weight and then washed with petroleum ether to remove traces of oil; by washing with hot water, any sodium hydroxide absorbed is removed. The filter is then dried at 105° and weighed, this weight being the coke value.

3. **To Determine the Tar-forming and Coke-forming Values,** the oil is heated 50 hours to 150° and then the tar and coke values are determined as in (1) and (2).

Kissling found the sum of the coke and the tar values to be for Pennsylvania oils from 0.2 to 0.5; for Russian oils, 1.2; for Texas oils, 2.2 to 2.8. The higher these values run, the more likely it is that the oil will change during use.

The methods of Kissling cause trouble with oils which have a great tendency to resinify; flocculent masses precipitate on treatment with alkali which make difficult the separation of the tar and coke bodies from the unattacked oil. Schwarz and Marcusson* therefore use the method described under transformer oils (page 162). At 120° no coke is formed so that only the tar value need be determined. The alkali layer is washed with 30 c.c. of low boiling naphtha to remove adhering oil; the benzol solution of tarry bodies is washed free from mineral acids. But washing the alkali layer with naphtha is objected to as tarry bodies dissolve, and the results are apt to be too low.

(*c*) **Oxygen Absorption.** The absorption of oxygen from air (or pure gas) is in part chemical and in part simple solution.

1. **Chemical absorption** generally takes place when a considerable surface is exposed. 0.3 to 0.5 gram of oil is spread over 1.0 to 1.5 grams of ignited pumice in a 30 to 40 cm. long and 20 to 30 mm. wide ignition tube and the tube then sealed, enclosing either air or pure oxygen; it is then heated several hours to the temperature in question (100°); the point is then opened under water (more exactly under mercury) at about 20° and the amount of oxygen absorbed determined (and reduced to standard conditions).

The chemical absorption of oxygen is very small even at 100°; two samples of kerosene (flash points 109° and 128° in the Pensky) absorbed no oxygen at 20° and with three hours heating, while a paraffin oil (water white in color) of flash point 158° and Engler viscosity 5.9 absorbed 2.4 c.c. per gram. In the case of kerosene, however, the absorption of even very small amounts of oxygen may cause a decided decrease in the quality especially under the influence of direct sunlight. Regarding the oxygen absorption of vaseline see page 253. Under the above conditions the oxygen absorption in the case of fatty oils and waxes is considerable. Sperm oil absorbs 14 to 25 c.c. of oxygen per gram at 100°, olive oil 33 to 34, raw rape oil 45 to 50 and cottonseed oil 69 c.c. of oxygen.

* Zeit. angewandte Chem., **26**, 385, 432 (1913).

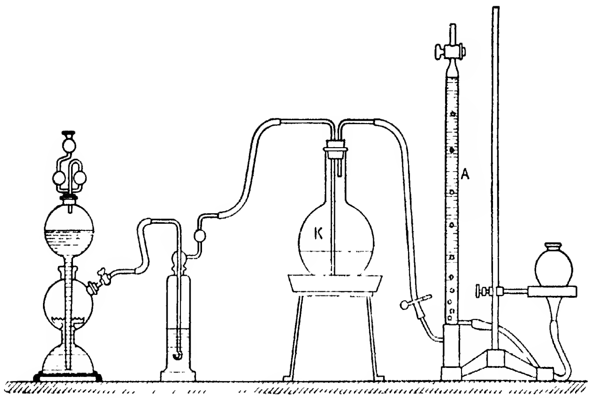


FIG. 101.

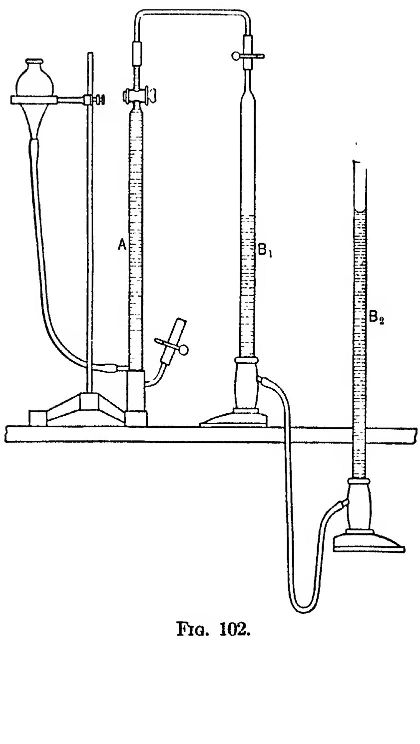


FIG. 102.

2. **Dissolved oxygen,** accompanied by traces of nitrogen, is found in all oils. The former specifications requiring oils to be not only free from acid and resins but also free from free oxygen are not clear in the light of the statement just made. The determination of free oxygen can be made as follows (Figs. 101 and 102):

Carbon dioxide gas is passed through a round-bottom flask containing 200 c.c. of oil until the bubbles of gas passing into the potassium hydroxide solution of specific gravity 1.32 are completely absorbed. The leading-in tube which up to this time has not gone below the surface of the oils is now pushed below the surface and the oil is heated to 150°. The gases driven from the oil are pushed by the carbon dioxide into the eudiometer tube. When again only carbon dioxide passes, the operation is finished. After standing two hours over the KOH, the gas is run into a Hempel gas burette (Fig. 102) B_1B_2 and after reading the volume, run into an oxygen absorption pipette filled with alkaline pyrogallol; after the oxygen has been absorbed, the gas volume is again determined; the difference in volume is oxygen. The volume is calculated to 0° C.

Four compressor oils examined contained in 100 c.c. 4 to 5 c.c. of air or the following amounts of oxygen: 0.9, 1.1, 0.7, 1.4 c.c.

XV. Corrosive Action

(*a*) **Machine Oils.** The corrosive action of mineral oils free from acid on the bearing metal is practically negligible. Comparative tests are made as follows:

Weighed polished plates of the metal covered with oil are heated for a long time to 50° and protected from dust. From time to time, after cleaning the plates with filter paper and ether, any changes in appearance and weight are determined. The corrosive action of the oils on cement can also be neglected unless the oil contains acid.

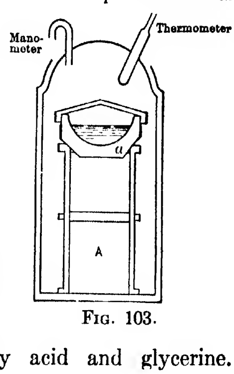


Fig. 103.

(*b*) **Steam-cylinder Oils.** The lubricating oils attack the metals with which they come in contact only when they contain fatty oil which is gradually decomposed under the action of the superheated steam into fatty acid and glycerine.

To determine the extent of the corrosive action 25 to 30 grams of oil are placed in an agate dish *a* (with a loose copper cover), resting on a copper tripod (Fig. 103) together with a polished, weighed cast-iron plate (30 × 30 × 3 mm.); the whole arrangement is then subjected to the action of superheated steam in the autoclave *A* (Fig. 104). The alarm clock and the automatic pressure regulator keep the pressure

definitely at a certain value for a determined time. The loss in weight of the plate is determined. In the residual oil the amount of free acid may be determined in so far as it has not been changed to iron soaps. The time of experiment is usually 4 to 6 hours; if at that time no corrosion has taken place, it is prolonged to 10 hours.

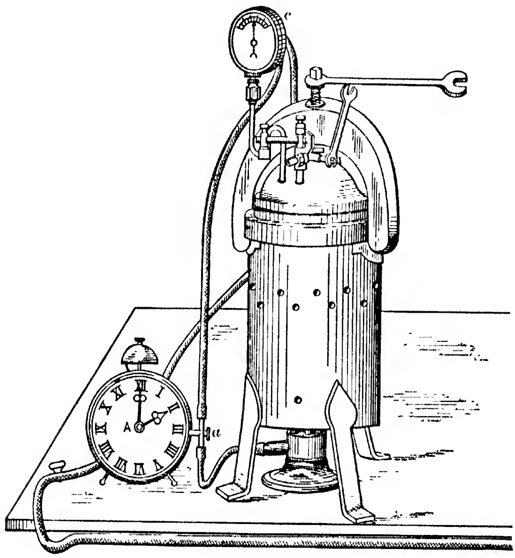


FIG. 104.

Table 46 gives the vapor pressure of water in atmospheres at different temperatures.

TABLE 46

VAPOR PRESSURES OF WATER IN ATMOSPHERES

°C.	Atmospheres	°C.	Atmospheres	°C.	Atmospheres
100	1.0	150	4 7	200	15 4
105	1.2	155	5 4	205	17 0
110	1.4	160	6 1	210	18.8
115	1.7	165	6 9	215	20.8
120	2.0	170	7 8	220	22.9
125	2.3	175	8 8	225	25 1
130	2.7	180	9.9	230	27 5
135	3.1	185	11 1	235	29.8
140	3 6	190	12 4	....	....
145	4.1	195	13.8	....	....

TABLE 47

CORROSIVE ACTION OF OILS ON CAST IRON UNDER THE SIMULTANEOUS ACTION OF STEAM AT TEN ATMOSPHERES PRESSURE

Kind of oil	No. of sample	Loss in weight (milligrams) of the plates after heating, hours					Acid content of oil			
							Before heating	After heating, hours		
		2	4	6	8	10		6	8	10
Crude rape oil	1	−0.5	−9	−60	−183	−211	0.85	36.7	60.6	74.0
	2	−1	−7	−58	−160		1.20		58.5	....
	3	−2.4	−9	−42			1.20			....
Thickened or condensed rape oil	1			−224						....
	2			−197						....
Refined rape oil	1	−12	−81	−276			0.35	64.2		..
	2	−16	−81	−217			1.34	69.1		
	3	−0.5	−0.5	− 7	−80			18.3	46.5	
90 parts dark mineral oil, 10 parts fatty oil		−0.5	−1	−1			1.0			
Mineral spindle oil		−2.7	−3.4	−4			0.075			
Mineral wagon oil		−4	−4	−1			1.28			
2 volumes mineral oil, 1 volume rape oil		+0.2	−0.9	0						
Cylinder oil (mineral) with 20 per cent rape oil		−1.4	−1.6	−1.4						.
Mineral cylinder oil with 6 per cent of bone oil				−6			0	0.85		.

(*c*) **Corrosive Action on Cement and Concrete.** Cement and concrete are resistant to the action of tars and mineral oils. Concrete reservoirs for mineral oils have been found satisfactory; fatty oils on the other hand have a decomposing action on cement and concrete, probably because of the presence of fatty acids.*

XVI. WATER

(*a*) **Qualitative.** See page 72. Cloudiness in pale oils, see page 173.

(*b*) **Quantitative Determination.** 10 to 12 grams of the well-mixed oil are heated on a water bath with stirring until the foam on the surface has disappeared; if the oil contains much water 3 to 5 grams (mixed with 10 to 15 grams of oil, dried with calcium chloride and then filtered) are used. At the same time an approximately

* Tonindustrie-Ztg., **1912,** Nr. 100.

similar amount of dehydrated oil is heated till the foam disappears. After cooling, the loss in weight of the original oil minus the loss in weight of the dehydrated oil gives the amount of water in the original oil. With non-volatile steam-cylinder oils the blank test may be omitted.

The method for crude oils described on page 72 may be used for lubricating oils containing much water as well as easily volatile substances. The latter method has been found useful in the examination of cylinder oils purified by the Friesdorf oil separator.

XVII. Ash

This determination is generally unnecessary if the oil is completely soluble in naphtha or in benzol and if the aqueous and the hydrochloric acid extracts of the oil show no appreciable residue on evaporation. In a more exact examination of the lubricating oil a determination of the ash is necessary. Imperfectly purified oils generally contain small amounts of alkali soaps (0.1 to 0.2 per cent of ash), which is made evident by their hydrolysis on shaking the oil with water or alcohol containing phenolphthalein, a red color appearing. Refined machine oil should contain at the most 0.01 per cent of ash (cylinder oil, 0.1) which should not, however, contain any alkali.

For the determination of ash, see page 73.

XVIII. Addition of Soap

To increase the consistency of mineral oils, aluminum and alkali soaps are added in many cases, the latter in order to give the power of emulsifying with water (see water-soluble oils). Traces of soap, formed by the alkalies acting on naphthenic acids during the refining, remain in the oil if it is imperfectly purified. The oils should be washed till free from soap.

(*a*) **Qualitative Detection.** 1. The presence of alkali soaps is shown by the formation of white, slimy emulsions on shaking with water. These fine emulsions may be distinguished from the cloudiness caused by shaking with water oils containing mucin, by the fact that on the addition of phenolphthalein a red color will appear because of the hydrolysis of the soap; furthermore by treatment with mineral acids the emulsion immediately disappears because of the decomposition of the soaps. In the hydrochloric acid solution sodium and potassium can be detected as usual. Ammonium soap is detected in the original oil through its spontaneous decomposition into ammonia and fatty acids. Calcium and aluminum soaps are detected by testing the hydrochloric acid extract of the oil for aluminum and for calcium.

(*b*) **Emulsification Test.** 10 c.c. of oil and 10 c.c. of water are shaken at 85° for 1 minute in a 20 mm. wide test tube. An oil is considered as non-emulsifying if it separates after standing one hour at 85° and if a layer less than 1 mm. thick has formed between the oil and water; and as weakly emulsifying, if a 2 mm. layer forms. If the oil does not separate from the water or if a layer thicker than 2 mm. forms, it is emulsifying. Care must be used in interpreting the result.

Another test is suitable for machine oils at room temperatures:

10 c.c. of oil and 10 c.c. of distilled water are shaken in a 25 c.c. graduated cylinder for 5 minutes at room temperature. After standing one hour, the degree of separation into layers is noted.

(*c*) **Quantitative Detection.** 1. By this method the fatty acids are liberated by the addition of mineral acid; if these fatty acids are not soluble in water, the mineral acid can be washed out.

10 c.c. of oil are shaken in a separatory funnel with 100 c.c. of ether and an excess of hydrochloric acid; the lower aqueous layer is run off and twice extracted with 30 c.c. portions of ether, the ether solutions (the water solution is examined for basic radicals) being then united and washed first with concentrated Glauber salt solution and then twice with a little distilled water (to break up emulsions, the amount of ether is increased or, without shaking the liquid, a small amount of alcohol is run in) till the wash liquid no longer reacts with silver nitrate. With pale oils, 30 c.c. of neutral alcohol are added and the free acid titrated in the presence of phenolphthalein. With dark oils, the ether is distilled off, the residue shaken with 20 c.c. of hot alcohol in a graduated cylinder, and, after separating the layers, the acid in the alcohol layer is titrated.

The total amount of fatty acids can thus be determined; by subtracting from this the amount of acid originally present in the oil the amount equivalent to that combined in the soap is determined. If the base of the soap is determined in the mineral acid extract and the molecular weight of the separated fatty acids is known, it will be possible to calculate the amount of soap in the original oil.

To determine the molecular weight of the fatty acids, the solvent is evaporated and the residue dissolved in boiling petroleum ether and 50 per cent alcohol. The mineral oil is then removed by the method of Spitz and Honig (page 197). The fatty acids are (page 198) liberated from the soap solution and their saponification value determined. The molecular weight (M) is obtained as follows:

$$M = \frac{56110}{\text{Saponification Value}}$$

Example: If the molecular weight of the fatty acids was 300, and the acid value of the fatty acids present as soap was found to be 28, and calcium was found to be the basic radical in the soap, then the amount of soap present may be calculated as follows:

$$2\text{KOH} : \text{Ca soap} :: 28 : X$$

$$112.22 : 638 :: 28 : X$$
$$X = 159.2 \text{ milligrams of soap or } 15.92 \text{ per cent.}$$

For sodium soap the expression would be:

$$KOH : \text{Na soap} :: \text{acid value} : X$$
$$56.11 : 322 :: 28 : X$$
$$X = 160.7 \text{ milligrams of soap or } 16.07 \text{ per cent.}$$

If the per cent of soap is less than five, the molecular weight of the fatty acids may without appreciable error be assumed equal to 300, and the difficult experimental determination be avoided.

2. In the presence of alkali soaps of water-soluble acids (for example, naphthenic sulpho-acids) the oil is repeatedly extracted with 50 per cent alcohol, the alcoholic layer separated, treated with a few c.c of low-boiling naphtha and the soap solution, now free from oil, evaporated; the weight of the residue gives the amount of soap directly.*

XIX. Content of Fatty Oil

(*a*) **Qualitative Test.** See page 75.

(*b*) **Quantitative Determination. 1. Volumetric Determination of the Saponification Value.** The saponification value is the number of milligrams of KOH necessary for the saponification of 1 gram of oil.

According to the amount of fatty oil suspected to be present 4 to 10 grams of the sample and 25 c c. of benzol free from sulphur are boiled for ½ hour with 25 to 60 c.c. of $\frac{N}{1}$ alcoholic potash under a reflux condenser and the excess of alkali is titrated with $\frac{N}{2}$ hydrochloric acid after adding 50 c c of neutralized absolute alcohol. The addition of benzol facilitates the action of the alkali on the fat. All vessels should have been previously rinsed with neutralized alcohol. A blank test with the alkali is carried on with each determination. The method of calculation is shown by the example. *Example.* Amount of substance used 10 grams; in the blank test 46.85 c.c. of $\frac{N}{2}$ HCl were required; with the oil 43.30 c.c. were required to titrate back; 3.55 c c. of alkali were thus required to saponify the fat. But 1 c.c. of $\frac{N}{2}$ HCl is equivalent to 28.055 milligrams of KOH. The saponification value is therefore $\frac{(3.55)\ (28.055)}{10}$ or 9.96.

For the fatty oils added to mineral oils the saponification value may be taken as 185, for mineral oils it is zero; if therefore a saponification value of 92.5 is found 50 per cent of oil is present, if the saponification value is found to be 18.5 then 10 per cent of fatty oil is present. In general the per cent of fatty oil may be calculated from the saponification value by the proportion.

$$185 : 100 :: \text{saponification value} : \text{per cent of fatty oil.}$$

* Marcusson, Chem. Umschau, **25**, 2 (1918).

If only the amount of neutral fat and not the amount of fatty acid is to be determined, in each case the amount of KOH necessary to neutralize the free acid in the oil is to be subtracted from the saponification value. If wool fat or sperm oil (or similar waxes), have been added, these being generally detected by their odor, the saponification values of these substances (105 on the average) should be used.

The volumetric determination of the amount of fatty oil is exact only when the saponification value of the added fatty oil is known; more exact is the following:

2. Gravimetric Method of Spitz and Hönig. The fatty oil is changed to soap soluble in alcohol; the unsaponifiable matter is extracted with naphtha.

(*a*) **In the Absence of Waxes.** 10 grams of the sample, 25 c.c. of benzol and 25 c.c. of 2 N alcoholic potash are boiled under a reflux condenser for 1 hour; the mixture is then treated with 50 c.c. of water and again boiled After cooling, the soap solution is transferred to a separatory funnel washing the last portions into the funnel with 50 per cent alcohol and about 50 c.c. of low-boiling naphtha (30 to 50°); after shaking and settling, the alcoholic solution is run off. The soap solution is shaken with 50 c.c. portions of naphtha until the last extract on evaporation gives no oily, but at most, traces of a soapy residue. The united naphtha extracts are three times shaken with 15 c.c. portions of 50 per cent alcohol to which has been added a trace of alkali; this alcohol, after having been shaken once with naphtha, is added to the soap solution. The naphtha solution is evaporated and the residue heated to dryness on a water bath in a weighed dish till all odor of the solvent has disappeared. If the residue should contain a few drops of water, it is stirred up with 5 to 8 c.c. of absolute alcohol and heated till all odor of alcohol has disappeared, the alcohol being evaporated when the bubbles of foam on the surface have disappeared. The mineral oil is then dried for 5-minute periods at 100° till constant in weight to 1 to 2 milligrams. The difference between the weight of the mineral oil separated and the weight of the original oil gives the weight of the fatty oil plus the amount of fatty acids.

If, for example a mixture of fatty oil with a volatile mineral oil is under examination (as, for example, a mixture of rape and kerosene oils used for lanterns), the drying of the unsaponifiable matter according to the method of Spitz and Honig may cause a loss of material In such a case after distilling off the main quantity of naphtha, the dish with the residue is heated until no more bubbles escape, the cooled dish being weighed after standing for a short time. According to Holde it is also possible to mix the oil mixture with a definite weight (10 grams) of ceresine, this being then heated on the water bath to constant weight; the ceresine holds back the volatile kerosene.

In the presence of large amounts of unsaponifiable oil or difficultly saponifiable fat (tallow, etc.,) it is better to test the unsaponifiable matter for fat by the method of page 76, and if necessary, an aliquot part is again treated to obtain the completely purified unsaponifiable matter.

After evaporating off the alcohol from the soap solution, the residue can be used for a qualitative and quantitative examination of the fatty acids (see below).

(*b*) **In the Presence of Wool Fat and Waxes.** In the presence of these substances the higher alcohols obtained from these bodies are separated with the unsaponifiable matter. They are separated from the unsaponifiable matter by two hours digestion with acetic anhydride under a reflux condenser; the alcohols are esterified and pass into the acid solution and, after being washed with acetic anhydride into a separatory funnel, are separated from the mineral oils. The separated mineral oil is freed from dissolved acetic anhydride by washing with dilute alkali in petroleum ether solution. Some of the mineral oil (3 to 5 per cent) passes into solution along with the esters and must be considered in the calculation. Since wool fat and waxes themselves contain varying amounts of hydrocarbons (10 to 53 per cent) and since the saponification of the wool fat when boiled with alcoholic potash is probably incomplete, it follows that a quantitative analysis of mineral oil in the presence of wool fat or waxes must be only an approximation. For the determination in the presence of solid waxes, see page 520. If the unsaponifiable material consists of paraffin or ceresine, the melting point will be unchanged after acetylization; in the presence of higher alcohols, the melting point will sink, as the acetates have a lower melting point.

(*c*) **Determination of the Nature of the Fatty Oil.** The alcoholic aqueous soap solution obtained by the method of Spitz and Honig is evaporated till the odor of alcohol disappears; the residue, dissolved in little water, is treated with excess dilute sulphuric acid in the presence of petroleum ether in a separatory funnel. The acid layer is run off and the resulting fatty acid solution is washed with conc. Glauber's salt solution and twice with distilled water till the wash water does not turn methyl orange red. The petroleum ether is dried for a short time with calcium chloride, filtered and distilled and the residual fatty acids are dried 5 minutes at 105°. Insoluble oxy-acids separate between the acid and petroleum ether solutions or on the walls of the separatory funnel.

From the presence of oxy-acids, which occur in large amounts in castor oil, in oxidized or blown oils and in fish oils (page 413) conclusions may sometimes be drawn regarding the nature of the sample of oil. The insoluble oxy-acids are isolated by decantation or filtration with subsequent solution in alcohol. The acids soluble in ether, after sufficient drying, are examined as to their iodine value, molecular weight (see page 400) and melting point. From these data the nature of the oil is determined according to page 422. In cases of doubt the origin of the oil (whether animal or vegetable) is determined by the method of page 399.

XX. Added Unsaponifiable Oils

(*a*) **Rosin Oils.** 1. **General.** In the distillation of pine resin with steam there is obtained a volatile turpentine oil and a residue called colophony. When colophony is distilled from retorts there is obtained (besides the volatile, mobile rosin spirit or pinolin) a heavy rosin oil boiling above 300°. Crude rosin oil contains (besides at times as much

as 30 per cent of acid rosin, mechanically carried over) hydrocarbons,* mainly retene derivatives. Crude and refined rosin oils are used as transformer oils, in making wagon greases, in cutting lubricating oils and varnishes and in the preparation of water-soluble oils. Because of their tendency to resinify (in thin layers they become solid or sticky after 24 hours) rosin oils are considered to be poor lubricants. As the following table shows, they evaporate more easily than do mineral lubricating oils and consequently the flash point of rosin oils is lower than with mineral oils. They can be easily distinguished from mineral oils by their characteristic odor and taste.

TABLE 48

	Loss on evaporation in per cent after heating		Flash point, °C.	
	5 hours at 100°	2 hours at 170°	Pensky	Open vessel
Heavy rosin oil.....	0 40 to 0 80	5 6 to 7.4	109 to 146	148 to 162
Mineral spindle oil. .	0.05 to 0.10	0 5 to 1.8	177 to 203 (one oil 121)	189 to 213
Mineral machine oil	0 06 to 0.13	0.6 to 1.1	188 to 195 (one oil 126) (one oil 139)	205 to 221

2. **Color Reactions** (α). On shaking equal volumes of oil and of sulphuric acid of specific gravity 1.6, the mixture assumes a red color, the acid separating with a blood red color. By means of this reaction 1 per cent of rosin oil can be recognized; very carefully purified rosin oils give the reaction only faintly or not at all.

(β) If 1 c.c. of oil and 1 c.c. of acetic anhydride are shaken vigorously, the acid layer separated and 1 drop of sulphuric acid of specific gravity 1.53 added to this acid layer, a violet color will develop in the presence of rosin oil. (Storch-Liebermann reaction.) This reaction is sharper than the one just given but is also caused by rosin. In the presence of free rosin, rosin oil is detected by methods 3 to 7 as well as by its odor.

If rosin oil by itself or in carbon disulphide solution is shaken with tin tetrachloride (according to Allen tin bromide is better), a violet color will develop.

3. **Solubility in Alcohol and in Acetone.** Of rosin oil, 50 to 100 per cent is soluble in two volumes of absolute alcohol, of mineral lubricating oils only 2 to 15 per cent, of lighter lubricating oils as much as 35 per cent may dissolve. Rosin oil is miscible in all proportions with

* Chem. Ztg., **24**, 1105 (1900); Arch. f. Pharm., **1903**, 523–545.

acetone; mineral oil requires several times its own volume to dissolve.

4. **The Index of Refraction** of rosin oils at 18° ranges from 1.535 to 1.550, of mineral lubricating oils generally from 1.475 to 1.517, while American light machinery oils of specific gravity 0.852 to 0.880 have the index of refraction ranging from 1.476 to 1.489 (determination of Dr. Brauer).

5. **Optical Rotatory Power.** Mineral oils rotate very little; $[\alpha]_D$ is at most* + 3.1°, often it is zero. With rosin oils, however, $[\alpha]_D$ ranges from + 30° to + 50°; with oils from which the acid has been removed, the rotatory power may drop to + 23°.

6. **The Specific Gravity** of rosin oils ranges from 0.97 to 1.00, with mineral lubricating oils, 0.840 to 0.940, as a rule 0.880 to 0.915 at +15°.

7. **The Iodine Value** of rosin oils lies between 43 and 48, with mineral oils generally under 6, rarely over 14, with crack distillates, it may run decidedly higher, up to 70.

If from the color tests rosin oil may be suspected, the properties mentioned under procedures 3 to 7 are determined with the original oil and, if necessary, also with the alcohol-soluble portion of the oil; this extract should show the properties of the rosin oil to a still stronger degree.

8. **Quantitative Determination of Rosin Oil Mixed with Mineral Oil.** According to Storch, 10 grams of oil free from fat are gently warmed with 50 grams of 96 per cent alcohol and shaken. The decanted, cooled liquid, after washing the remaining mineral oil with some 96 per cent alcohol, is put into a weighed Erlenmeyer flask and freed from alcohol by heating on a water bath. The residue A is weighed and treated with 10 parts by weight of alcohol; the rosin oil is thus dissolved, the solution then evaporated and the residue weighed (B). The mineral oil dissolved in B is calculated as follows: If to dissolve the 10 grams of substance a grams of alcohol were used, and if for the solution of A, b grams were required, then $a - b$ grams of alcohol will dissolve $A - B$ grams of mineral oil; therefore b grams of alcohol dissolve $\frac{A - B}{a - b}(b)$ grams of mineral oil; this amount is to be subtracted from the weight B, to obtain the correct amount of rosin oil.

9. **Qualitative Detection of Heavy Mineral Oil Mixed with Rosin Oil.** A simple test for mineral oil when mixed with rosin oil (according to Valenta) consists in shaking 2 c.c. of oil with 20 to 22 c.c. of a mixture of 10 parts by weight of alcohol (91 per cent) and 1 part of chloroform. If a cloudiness develops, due to the formation of oily drops, or if an oily layer separates, then mineral oil is present.

Mineral oil has no characteristic reactions, the solubility tests giving no sharp indication of the presence of small amounts (under 15 per cent) of oil. For a more certain recognition of small amounts of

* Rakusin, Chem. Ztg., **28**, 574 (1904).

mineral oils there is used the method of Holde, depending on the difference in solubility of mineral and rosin oils in alcohol, and the difference in the index of refraction.

10 c.c. of oil are shaken in a glass-stoppered measuring cylinder with 90 c.c. of 96 per cent alcohol at room temperature. The presence of traces of undissolved material is of no significance. (Case I.) If considerable amounts of oil remain undissolved (Case II) the presence of mineral oil may be at once suspected. This suspicion is confirmed by allowing the mixture to stand (over night) and examining the separated oil, after washing with a little alcohol, in a refractometer to determine its index. In the presence of mineral oil, the index of refraction is less than 1.5330 at 18°. In this case, as in Case I, the separated oil can be further treated and tested.

In Case I the alcoholic solution is treated with water till a milky cloudiness results. After standing over night, the clear solution is poured off from the oil drops which should not, however, occupy more than 1 c.c.; the residue still clinging to the oily drop is washed with 96 per cent alcohol and then the oil is dissolved in 20 c.c. of 96 per cent alcohol at room temperature. By adding water to this solution a cloudiness again results and oil is separated (not more than 0.1 c.c.); this is washed with alcohol and then transferred to a small dish. After evaporation of the alcohol and cooling of the drop to room temperature, the refractive index is determined. If this is under 1.5330, then mineral oil may be assumed to be present.

(*b*) **Coal-tar Oils.** The oils in question are dark oils obtained by pressing anthracene; they can be recognized by the following properties:

Their specific gravity is over 1.0, they are completely soluble in alcohol at room temperature, their odor is that of creosote, and sulphuric acid (conc.) dissolves them with the formation of water-soluble materials. They react violently with conc. nitric acid (sp. gr. 1.45), often explosively, with the formation of nitro derivatives. Their viscosity is low (at 20°, from 2.29 to 4.6 Engler degrees).

Coal-tar oils as well as other tar oils give the diazobenzol reaction for phenols recommended by Graefe.

The oil is boiled with $\frac{N}{1}$ aqueous sodium hydroxide and the alkaline extract (filtered if necessary) is treated cold with diazobenzol (freshly prepared by the addition of potassium nitrite to a solution of anilin hydrochloride cooled with ice); in the presence of phenol or creosote-containing oils an intense red color will develop (see also page 268).

To distinguish coal-tar oils from mineral oils the Valenta* test is useful. This depends on the fact that benzene hydrocarbons, as they occur in coal-tar, are soluble in dimethyl sulphate while crude oil, naphtha, kerosene, mineral oil and rosin oil remain undissolved.

* Chem. Ztg., **30**, 266 (1906).

In a measuring cylinder a definite amount of oil is shaken with 1.5 to 2 volumes of dimethyl sulphate for 1 minute and after separation of the layers the difference in volume is observed. (Danger! Dimethyl sulphate is poisonous!)

Graefe* found that this method gave almost theoretical values with mixtures of high-boiling coal-tar and mineral oils; only in the case of low-boiling petroleum distillates is there a decided solubility in dimethyl sulphate, and with lignite tar oils a constant error of 10 per cent results. This difference in solubility might allow a separation of coal-tar and lignite-tar oils.

(*c*) **High-boiling Lignite Tar Oils.** These have an odor like creosote and a specific gravity from 0.89 to 0.97, 22 to 62 per cent being soluble at room temperature in two volumes of alcohol. They contain considerable amounts of sulphur (see page 302), and react more vigorously with nitric acid of specific gravity, 1.45 (because they contain considerable amounts of unsaturated hydrocarbons with iodine values up to 70), than do mineral oils, but less vigorously than do the coal-tar oils; they have as a rule an Engler viscosity of 1.6 to 3.0 at 20° (rarely as much as 30). Nearly all give the diazobenzol reaction.

(*d*) **Beech-wood Tar Oil** is recognized by its peculiar, penetrating, characteristic odor; its specific gravity is close to 1.0. It is completely soluble in alcohol, like coal-tar oils. It gives the diazobenzol reaction for phenols. A sample of a grease for hoisting ropes showed a specific gravity of 0.991, an Engler viscosity of 228 at 20°, a flash point of 84° and contained 20 per cent of viscous mineral oil and 80 per cent of beech-wood tar, added as a preservative; the latter was separated from the mineral oil by extraction with alcohol.

XXI. Dissolved Rubber

Unvulcanized rubber† has been added in small amounts (1 to 2 per cent) to lubricating oils to increase their viscosity and slipperiness; the rubber may generally be recognized by the stringiness of the oil but this must not be confused with the very similar phenomena exhibited when soaps are present.

A very sticky oil was dissolved in ether; by adding alcohol (till proportions were, 4 ether, 3 alcohol) two per cent of rubber was precipitated.

Tests made with this oil on a Martens oil-testing machine gave a mean frictional coefficient of 235 (rape oil = 100). With pressures of 10 to 25 kilograms per square centimeter, disturbance of lubrication was observed; with pressures of

* Chem. Rev., **14**, 112 (1907).

† Colemann, Eng. Patent of Dec. 30, 1870; Ber., **4**, 812 (1871). D. R. P. 55,109, Oct., 1895, W. H. Lepenau, Salzbergen.

35 to 80 kilograms per square centimeter the lubrication was incomplete; the temperature of the bearings rose rapidly although the machine was working under the most favorable conditions, that is, with complete lubrication through immersion in a bath of oil. Although the oil during the test was at times completely thrown away from the shaft it always returned again to the bath because of its stringiness. Heated to 100°, the oil lost its stickiness and stringiness but regained these properties on cooling; the cooled oil had an Engler viscosity of 78 at 20°. However on heating to 150° and cooling, the rubber did not at once separ te from the oil on treatment with alcohol-ether (3 : 4); but on gently heating, a brown flocculent precipitate of the rubber substance appeared. The oil, after cooling and treatment with ether-alcohol (1 : 1), gave a cloudy solution which was no longer stringy and sticky; it was decidedly more mobile (Engler viscosity at 20° was 46.5); in other words a deep-seated transformation had taken place both as to physical properties and as to precipitability from ether (depolymerization of the rubber). Experiments carried on under the same conditions as above with some of the oil from which the rubber had been removed gave a frictional coefficient of 113 (rape oil 100) with no disturbance of the lubrication up to pressures of 145 kg. per square centimeter. The oil free from rubber showed the normal properties of pure, heavy mineral machine oils.

(*a*) **Precipitation in Ether Solution by Means of Alcohol.** A solution of 10 grams of oil in 20 c.c. ether is treated with enough alcohol (say 40 c.c.) to effect sufficient precipitation of rubber and yet not cause a separation of oil. (Soaps which might be precipitated by the alcohol are first to be decomposed by hydrochloric acid, the acid and resultant chlorides being washed out, before the alcohol is added.) After standing for some time, the rubber will settle and it can then be filtered, washed with alcohol-ether (1 : 2), dried and weighed.

(*b*) **Method of Budde as Modified by Hinrichsen-Kindscher.*** In place of the method of Budde† the Materialprüfungsamt has worked out the following provisional method.

Most of the oily matter can be separated from the rubber by one treatment with acetone. 0.1 gram of the residue is allowed to swell in 15 c.c. of chloroform, 10 c.c. of a bromine solution (containing 5 c.c. of bromine in 100 c.c. of chloroform) are added and the mixture is allowed to stand 5 hours in ice water. It is then transferred to a beaker, being washed into this with chloroform. Three to four volumes of naphtha are added quickly and the precipitate is filtered at once. The precipitate is washed with alcohol till white and the washings appear colorless. The washing is then continued with hot water, then with alcohol and ether. The dry filter is fused with a mixture of sodium and potassium carbonates without heating the material above redness. The fused mass is dissolved in water and acidified cold with nitric acid, silver nitrate is added, the solution heated to boiling, the precipitate collected on a paper and the silver bromide determined as usual. The amount of rubber is calculated from the amount of bromine found by multiplication with 0.425 (319.7 Br is equivalent to 136.1 of rubber $C_{10}H_{16}$).

* Hinrichsen, Materialprüfungswesen, Springer, Berlin.

† Gummi Ztg., **24**, 4 (1909).

XXII. Suspended Substances

(*a*) **Accidental Mechanical Impurities** can be seen in pale oils by inspection; in dark oils they can be detected by pouring through a sieve of $\frac{1}{3}$ mm. mesh and then washing the latter with ether.

For qualitative and quantitative tests, see page 73.

(*b*) **Asphalt (Benzol-soluble)** may be present in suspension (as well as in solution) in dark oils, together with insoluble mechanical impurities. The asphalt must be determined in filtered and in unfiltered oil, according to page 106; the difference is the amount of suspended asphalt. In a similar manner, the alcohol-ether insoluble suspended asphalt may be determined (page 106).

(*c*) **Vaseline, Paraffin, Soap, etc.** Besides the substances mentioned, there may be suspended in mineral oils some vaseline, paraffin particles, iron soaps, etc. The nature of these substances is determined after filtration. If the residue on ignition leaves iron oxide, iron soaps may have been present; fatty acids are separated by mineral acid.

For the determination of graphite suspended in oil, see page 237.

XXIII. Dissolved Asphalt and Dissolved Paraffin

These may be considered as normal components of mineral lubricating oils. The dark oils are colloidal solutions (in high-boiling hydrocarbons) of the asphalt contained in the crude oil or formed in the distillation.

The determination of asphalt is important in many cases (page 106) since its presence causes resinification and clogging of bearings and lubricating canals and may cause the formation of cylinder deposits; consequently in some specifications limits have been set as to the amount of asphalt (insoluble in naphtha) permissible in railway and cylinder oils. The amount insoluble in alcohol-ether is specified only in a few cases (see pages 216 to 217). The majority of samples examined in the Materialprüfungsamt contained less than 1.7 per cent of asphalt insoluble in alcohol-ether; only in rare cases did it reach 3.5 per cent. Asphalt is determined as described on page 106; but a determination is required only in the most careful analyses.

XXIV. Ceresine

Small amounts of ceresine are sometimes added to steam-cylinder oils, liquid at room temperatures, in order to obtain a salve-like consistency; it may be detected, in case the oil is not too dark, by the forma-

tion of a light-colored precipitate on adding 3 parts of alcohol to 4 parts of the ether solution of the oil. The white precipitate is to be filtered, purified by washing with alcohol-ether and the melting point determined in a capillary (it generally melts between 66° and 71°). An exact quantitative method has not yet been worked out. See also page 290.

XXV. Degree of Purification

This is generally sufficiently determined by the previous tests for acid, alkali, etc. A well-purified lubricating oil should be clear and transparent, should deposit no precipitate on standing for some time, nor should one form when the temperature is changed; it should contain no water, particles of rosin, sodium sulphate or dissolved naphthenic acid soaps.

The following is recommended by the International Committe on the Unification of Petroleum Analysis:

Inorganic salts are determined in the aqueous extract from 100 c.c. of oil. The presence of soap in pure mineral oil is shown by the permanent emulsion and faint alkaline reaction of the aqueous extract, in which the qualitative detection of alkali soap is made as follows: in a test tube 15 mm. wide, 0.5 c.c. of lye (sp. gr. 1.005) are heated to boiling. An equal volume of oil is then added and the mixture heated to boiling; the mass is kept in a boiling water bath for 2 to 3 hours. The oil must be clear in the absence of naphthenic acids and the alkaline extract must appear transparent so that small type is visible through it. Cloudiness points to a content of salts of naphthenic acids, in which case the ash must be determined.

The emulsion test of page 195 has recently been advised since oils which have not been carefully freed from sodium salts (alkali salts of sulpho-acids) easily escape from the cylinders with the steam and condensed water and thus cause a large waste of material and disturbance in using the condensed water again.

XXVI. Order of Tests

The order of tests depends on the specifications which are to be met by the oils (see Tables 49 to 53). With dark railroad oils, the cold test is made at once, since oils with improper temperature of solidification are at once excluded. Fatty oil, rosin oil, tar oil, water and mechanical impurities are often made evident by external appearance; the more exact determinations of these are made according to pages 75, 198, 71, 73 and 197. The determination of acidity according to page 69 is important. Light-colored mineral oils are generally free from acid; in dark oils, naphthenic acids are generally found.

If an oil is free from acid, the testing for rosin (colophony) will be unnecessary; with large acidity, tests according to page 200 should be made. *The solubility in "normal benzine" is only to be determined* in the case of dark oils (see page 106); the amount of alcohol-ether insoluble asphalt is generally determined only in the case of cylinder oils (page 106). The emulsion test (page 195) is sometimes required with cylinder oils. The other chemical tests from page 184 to page 223 are performed only in exceptional cases.

To determine the usefulness of lubricating oils for definite purposes the specific gravity, viscosity, flash point, fire test and cold test are determined. The specific gravity of machine and wagon oils is generally determined by hydrometer, of cylinder oils by pycknometer (pages 2 and 5). The determination of viscosity is made with machine oils at 20° and 50°, with cylinder oils at 50° and 100°. The flash point (at the Materialprüfungsamt) is always determined in the Pensky apparatus except when the open tester is definitely asked for. With regard to the cold test, it may be necessary to determine the behavior at a definite temperature (railroad oils) or to find out at what temperature it solidifies (page 35). The test with machine oils is made in the U-tube; cylinder oils are almost always tested in test tubes at 0°.

XXVII. Specifications for Lubricating Oils

The specifications of the different railways are much the same, although those of the smaller ones are perhaps not quite so rigorous, thus nothing may be said about the degree of purity or the content of asphalt, although mineral oils, so-called unrefined residues, are asked for. In Tables 49 to 53 will be found specifications of oils for a variety of purposes.

Specifications for Marine Lubricating Oils

The oil should be a mixture of mineral oil and fatty oil; an examination must show the fatty oil to be pure thickened rape oil. An analysis should show the following constants: Engler viscosity at 20° 38 to 44, at 50° 7 to 8; specific gravity at 15° 0.915 to 0.935 (water of 4° as 1); acid value (only organic acid) not over 3.5; mineral acids, rosin, rosin oil, tar oil, and impurities should be absent; on heating in a thin film for 10 hours at 50° there should be no change in the oil; the oil should remain liquid after exposure for 1 hour to − 10° C. in a test tube 15 mm. wide; the fatty acids separated from the oil should show an iodine value of 57 to 67 and a melting point not over 25° C.; the flash point in the Pensky-Martens apparatus should not be below 170° C.; the mineral oil isolated from the mixture should give an Engler viscosity at 20° C. of 22 to 25 and a specific gravity at 15° C. of 0.90 to 0.92; not more than 76 per cent mineral oil should be present.

The preceding specifications were in force during pre-war times. During the war, the producers, consumers, and interested scientific and technical experts collected data on the experience with the available materials in meeting the conditions imposed by the war. This resulted in the following regulations issued, with the assistance of the Raw Materials Section of the War Office, by the Scientific-Industrial Division of the War Lubricating-Oil Corporation.

Guidance for the Classification and Specification of Lubricants, with Regulations for Use of the Various Classes.

A. Classification.

B. Properties and characteristics of the various classes.

C. Regulations for the use of the different classes of lubricants, their requisition and release by the War Lubricating-Oil Corporation.

A. Classification

Lubricants are classified into:

I. Pure Lubricants from Petroleum.
  (*a*) Mineral Oil Distillates.
  (*b*) Refined Mineral Oils.
  (*c*) Residual Mineral Oils.

II. Pure Lubricants from Lignite and Shale.

III. Pure Lubricants from Coal Tar.

IV. Compound Oils.

V. Pure Greases:
  (*a*) Containing Soap.
  (*b*) Free from Soap.

VI. Filled Greases:
  (*a*) Containing Graphite or Soot.
    1. Containing Soap.
    2. Free from Soap.
  (*b*) Containing other Filling Materials.
    1. Containing Soap.
    2. Free from Soap.

B. Characterization and Properties of the Different Classes

I

(*a*) Mineral Oil Distillates are obtained by fractionally distilling petroleum; some of these products may be farther thickened by further volatilization of more volatile components. These materials show the following characteristics: The color may range from pale to dark, though the oil in the latter case will still be translucent in thin layers; there should be no mineral acids present; the oil should be practically free from water; it should dissolve in benzol without residue; a drop on a hardened filter should leave a translucent uniform spot, showing no separated particles.

(*b*) Refined Mineral Oils are obtained by careful treatment with sulphuric acid, sulphurous acid or other chemical reagents which separate acid, basic or resinous compounds. These materials show the following characteristics: They appear clear and translucent in a 15 mm. test tube; they should not contain over 0.1 per cent of acid, calculated as SO_3; they should be practically free from water; should be soluble clear in benzine.

(*c*) Residual Mineral Oils are products remaining behind in the stills during the first distillation of the raw material. They may be mobile, viscous, or salve-like. These materials show the following characteristics: The oils are dark colored, and only slightly or not at all translucent; the oils should be free from mineral acid; they should be practically all dissolved in benzol; a drop of oil on a hardened filter paper does not give a translucent uniform spot.

II

Pure Lubricating Oils from Lignite or Shale are obtained by distillation of the tars of these materials. These materials show the following characteristics: Specific Gravity under one; their odor suggests tar oil; they give the Graefe reaction .

III

Pure Lubricating Oils from Coal Tar.

(*a*) Tar Oils are obtained from Coal tar and should be as completely as possible freed from separating solid material (anthracene and similar bodies). Such materials show the following characteristics: The color should be dark brown or dark greenish brown; odor resembling that of coal tar; specific gravity at least 1.1 at 15° C. the oils should be practically free from water; they should be practically all soluble in benzol.

(*b*) Low temperature Oils. These are not yet defined; more experience with these is required.

IV

Compound Oils are obtained by mixing oils of classes I, II, or III or by adding other materials such as petroleum pitch, soft pitch or "goudron"; but coal tar or coal-tar pitch must not be added. The materials must be practically free from water and practically completely soluble in benzol.

V

Pure Greases. Greases are solid or salve-like at ordinary temperatures. They should be homogeneous and should not separate, nor dry up, in storage.

(*a*) Containing Soap. These should not contain more than 5 per cent of ash.

(*b*) Free from soap. Such greases should not contain more than 1 per cent of ash.

VI

Filled Greases. These may contain more than 5 per cent of ash.

(*a*) Besides soap, these may also contain graphite or soot.

(*b*) Other filling materials may be used, but should be acknowledged.

C. Regulations for the Use of Lubricants, their Requisition, and Release

I. The use of Oils in General.

Every industry should endeavor to use as few grades of oil as possible. A grouping of similar uses should be made; thus cylinder oil might be used for air-compressors, large gas engines, benzol-, petrol-, and gasoline-motors, and motor cars; or machinery lubricating oil might be used for large steam or gas engines, air compressors, for ring and drop oilers of dynamos, of steam engines, and of precision lathes. The oils are to be applied as follows:

(*a*) Mineral oil distillates are to be applied for the lubrication of bearings only when devices are available for keeping the oil constantly in use: a circulation system or a ring oiler. With other uses the spent oil draining off should be caught and after purification used again. Under no circumstances should mineral oil distillates be used where it is not possible to recover the used oil; however in the case of cylinder lubrication of internal combustion engines the use of such oils is permitted.

(*b*) Refined mineral oils are only to be used where chemical or physical influences produce in the oil decompositions, emulsions, oxidations, or resinification which it is necessary to avoid. For lubrication of bearings other than those of steam turbines, precision lathes and high velocity spindles refined mineral oil should not be used:

(*c*) Residual mineral oils, tar oils, coal-tar and shale oils and mixtures should be substituted for refined mineral oils wherever possible. The color and odor do not affect their application for lubrication. Mineral residual oils should also be used for cylinder lubrication.

II. Selection of Oils for Certain Purposes.

1. Cylinders, pistons and stuffing boxes of steam engines: mineral oil distillates or residual oils without addition of asphalt, hard or soft pitch. Flash point (according to the temperature of the steam), ranging from 200 to 270° in the open vessel; viscosity, at 100°, of an Engler degree above 2. Steam temperatures of over 300° should be decreased, since the available oils cannot resist such intensity of heat.

2. For cylinders, pistons and stuffing boxes of internal combustion engines (large gas engines, benzine-, benzol-, and gas-motor cars, petrol-, Dresel and crude-oil motors), vacuum pumps, blowing-engines: mineral oil distillates. Flash point: not under 180°, for low pressure compressors not under 160° in the open vessel. Viscosity: at 50° for small machines, the Engler degree should be about 4; for heavier machines, from 4 to 6 Engler degrees.

3. For circulating lubricating systems of larger units: mineral oil distillates. Flash point: over 150° in open vessel. Viscosity: at 50°, Engler degree between 3 and 4.

4. For ring oilers of all kinds of machinery: for sensitive bearings, mobile mineral oil distillates, for other uses, tar oils, mineral residual oils, compound oils. Viscosity: at 50°, Engler degree not over 4.

5. Drop oilers on all machinery: all not too viscous oils which contain no drying components.

6. For wick and pad oilers: all oils which contain no resinifying components.

7. For exposed lubricated surfaces, oiled directly from a can: mineral residual oils, tar oils, compound oils.

8. Ball-bearings: mineral oil distillates, or machinery greases containing no filling material or free inorganic components, unfilled solid greases containing soap.

9. Cooling and cutting oils (for automatic machines, for screws and small parts, bolts, for boring rifling, in the manufacture of various ordinance parts): Mineral oil distillates, of flash point over 140° in open vessel; viscosity at 50°, between 2 and 3 Engler degrees. Compound oils, mineral oil distillates with 10 per cent vegetable oil (rape oil), incorrectly called rape oil substitute. Flash point: over 140° in open tester. Viscosity: at 50°, between 2 and 3 Engler degrees.

10. Boring oil, for cooling of metal surfaces: Oils and fats emulsifiable with water.

11. Oil for protecting metals against rusting and during certain manufacturing processes: Mineral oil distillates, of flash point over 140° in open vessel. Viscosity at 50°, between 2 and 3 Engler degrees Compound oils, mineral oil distillates with not more than 10 per cent vegetable oil (rape oil) added, so-called rape oil substitute. Flash point: over 140°, in open vessel. Viscosity: at 50°, between 2 and 3 Engler degrees.

12. Oils for hardening and tempering metals (for munitions): shale oil distillates and mineral oil distillates. Flash point: over 170° in the open vessel, according to the particular use to be made of it. Viscosity: at 50°, between 3 and 4 Engler degrees. The flash point should be as high as possible, the viscosity as low as possible to allow most economical use.

13. For Compressors.

(*a*) Air compressors: For pressures up to 12 atmospheres: distillates, with flash point not under 160° C., in an open vessel. For high pressures (over 12 atmospheres) such as turbo-compressors: refined mineral oil, with flash point (in open vessel) 180° C. and higher according to pressure; for high pressure compressors, water-soluble oils also.

(*b*) For oxygen and hydrogen compressors: water-soluble oils.

(*c*) For refrigeration machinery: a refined mineral oil, liquid at − 15° C., viscosity at 50° of not more than 2 Engler degrees.

14. For steam turbines: refined mineral oils. Flash point: over 160° in an open vessel. Ash: not more than 0.03 per cent. Acid: not more than 0.02 per cent (calculated as SO_3). Emulsification test: must not emulsify.

15. For Switches: distillates. Cold test: according to use. Viscosity: at 20° C., not over 10 Engler degrees. Flash point: not under 140° C., in open vessel.

16. Transformer Oils: Preliminary Specifications of May 4, 1918. Refined mineral oil: Specific gravity, not under 0.85 and not over 0.92 at 15°. Viscosity: at 20° not over 10 Engler degrees. Flash point: not over 140° in open vessel. Cold test: must be liquid above + 5°. The oil must be free from alkali, salts and sulphur, and should contain not more than 0.02

per cent of acid, calculated as SO_3. It should be free from mechanical impurities, and should not contain suspended components, threads, sand, etc. The tar value after heating 70 hours at 120°, with a stream of pure oxygen bubbling through, must be not more than 0.8 per cent.

17. For spindle oils: refined mineral oils. Viscosity, at 20°, between 3 and 8 Engler degrees; flash point: at least 130°, in open vessel.
18. Greases Machinery greases, and greases for all cars running on rails or ropes: Groups V and VIa. Wagon greases: Groups Vb, VIa, and VIb.

Uses Not Mentioned

Special oils, needed for purposes not designated above, may be proposed: conditions of suggested use must be stated.

Compulsory Classification and Marking

On the bills to customers must be stated not only the trade name of the oil, but also the proper class for that individual material.

Example.

Dynamo oil, pure Mineral Oil Distillate Class Ia
Green Machinery Oil, a residual mineral oil. Class Ic.
Hardening Oil, Hindenberg grade, a shale oil distillate Class II.

BERLIN, *August* 15, 1918. LUBRICATING-OIL CORPORATION, INCORPORATED.

XXVIII. RECOVERED OILS

The oils used to lubricate the cold moving parts of machinery are often collected and, after more or less careful treatment, used again. The following points should help in deciding whether the recovered oil is like the original material and if it is still a sufficiently good lubricant. The used oils are at times darker and contain considerable water (up to 50 per cent) and mechanical impurities. If only traces of these impurities are present, the investigations may be the same as with any lubricant; otherwise water and mechanical impurities must be removed by heating for some time in a boiling brine solution, filtering through a hot water funnel and then if necessary drying with calcium chloride. With cylinder oils containing fatty oil, it is necessary to look for an increase in free acid (from decomposition of the neutral fat) and in iron soap and asphaltic substances. Specific gravity and viscosity of oils are increased in use through the evaporation of the more volatile portions.

TABLE

Specifications for Light-colored

		Engler viscosity at		Specific gravity at 15° C. × 1000	Cold test, liquid at °C.
		20°	50°		
A. Light machinery oils. Engler viscosity 4 to 25 at 20°, 1.9 to 5.0 at 50°. Solidification point I less than − 10 II less than − 5 III less than 0 IV less than + 5	Oils for refrigerating machinery	4.5 to 15	1.9 to 2.5	850 to 910	− 21
	Spindle oils	5 to 15	2 to 2.5	850 to 910	I − 10 II − 5 III 0 IV + 5
	For railway service	10 to 20	.....	903 to 918	− 15
	Steam turbine oils	9 to 13	2.6 to 2.9	...	I − 10 II − 5 III 0
	Air-compressor oils	9.5 to 22	2.7 to 4.9	870 to 900	I − 10 II − 5 III − 0
		At least 10	.....	870 to 900	
B. Heavy machinery oils. Engler viscosity 25 to 60 at 20°, 4.5 to 8 at 50°. Solidification point I less than −10 II less than − 5 III less than 0 IV less than + 5	Oils for bearings of cold moving parts of steam engines, dynamos, gas engines, etc.	15 to 25	2.5 to 4.5	860 to 910	.....
		30 to 40	5 to 7	900 to 915	....
	Dynamo machines	....	6 to 8	875 to 940	......
	Oils for bearings	....	5 to 7	903 to 928	− 10
		38 to 51	6 to 7.5	907 to 909	− 10 rarely higher
		....	Not under 6	908 to 920	....

49

MACHINE OILS (PURE MINERAL OILS)

Acid value calculated as per cent oleic acid	Flash point above			Remarks
	Pensky	Open vessel		
Less than 0 07	145	.	.	. . ..
Same	140			The typical Russian spindle oil, Nobel II, has an Engler viscosity at 20° C. of 12.3; at 50° of 2 97, flash point (Pensky) of 171°, solidification point − 15°, specific gravity 0.900.
Same	160		Prussian Railways, 1907	. . . . .
Same	175			* More viscous oils of viscosity 31.7 at 20° and 4 6 at 50° have been found practicable.
Same	200			For the lubrication of compressors (as of ammonia refrigeration machinery) very mobile mineral oils are used as they come in contact only with the cooled walls of the cylinders; under other circumstances, viscous oils of very high flash point are used, since the high compression in the presence of an oxidizing agent may cause ignition (and explosion), while mobile oils would be volatilized, in some cases aqueous glycerine or soapy water is used for lubrication.
	160		Bavarian Railways, 1907	
Less than 0 07	. . ...	200	Prussian Railways, 1907	. . .
Free from acid	175	. .	Bavarian Railways, 1907	. . . .
Less than 0 07	190	. . . . .	Royal Powder Works, Spandau, 1911	. . . .
Less than 0 21	160	.. .	Same	The typical Russian heavy machinery oil, Nobel I, has viscosity 41 at 20°, and 6.6 at 50°, Pensky flash point is 213°; specific gravity 0 907 and solidification point under − 10°.
Less than 0.07	193 to 201	. ...	..	Oils found satisfactory in practice.
Same	180	....	Imperial Wharves, Wilhelmshaven	. . . .

TABLE

PROPERTIES OF COMPOUND

		Engler viscosity at		Specific gravity at 15° × 1000	
		20°	50°		
....	... .	20 to 30	4 to 6	910 to 930	. .. .

TABLE

PROPERTIES OF LIGHT-COLORED MINERAL

		Engler viscosity at		Specific gravity at 15° × 1000	Solidification point liquid at °C.
			50°		
C. Gas engines	(a) Oils for small and large gas engines	12.4 to 77	3.4 to 8 2	.. . .	I less than −10 II less than − 5 III less than 0 IV less than + 5
	(b) Oils for gas engines of 1000 H.P.	77 to 130	8 to 15	.	Same
D. Diesel motors	For cylinder and air pump	....	9 to 10	. .	−5
	For the bearings		At most 7		− 10
E. Automobile oils*	Viscous motor oil (summer)	42 to 80	7 to 11	880 to 940	. ... ..
	Mobile motor oil (winter)	20 to 42	4 to 7	870 to 940	− 12
	For the cylinders	20 to 85	4.4 to 10 8	....	. ...
	For cylinder and driving mechanism	....	8 to 15	....	....

50
MACHINE OILS

Acid value calculated as per cent oleic acid	Flash point			Remarks
	Pensky-Martens	Open vessel		
Not more than 1.06	175°	.	Bavarian Railways, 1910	Purest light-colored mineral oil with at least 10 per cent rape oil, free from water and mechanical admixture

51
LUBRICATING OILS FOR EXPLOSION MOTORS

Acid value calculated as per cent oleic acid not more than	Flash point not below °C			Remarks
	Pensky-Martens	Open vessel		
0.07	190 to 211, rarely below 170			Oil of viscosity 16.4 at 20° and flash point (open vessel) 218° was found practicable for motors of 2.8 H.P., an oil with 3 per cent bone oil and viscosity 23.4 at 20°, flash point 196 (O.V.) for motors of 150 H.P.
0.07	210			
0.07		220		Not more than 10 per cent of material destroyed by conc. sulphuric acid
0.07		180		Same
0.00		210		Transparent clean mineral oil.
0.00		195	.	Same.
0.07	185 to 215**		General experience of the K. Materialprufungsamt	* Automobile oils should not have too high a boiling point since a portion of the lubricant always burns in the cylinder; the higher its boiling point, the less completely it burns. According to Schwarz and Schlüter [Chem. Ztg., **35**, 413 (1911)] on treatment with acetone, that part which is insoluble is a good automobile oil, while the acetone soluble portions burn incompletely and give a bad odor to the products of combustion. **In some cases 175.
0.07	206 to 240		Same	....

TABLE

PROPERTIES OF DARK MINERAL OILS

		Engler viscosity at		Specific gravity at 20° C. × 1000	Behavior in cold. Rise in 6-mm. U-tube at least 10 mm. at ° C.
		20°	50°		
Summer oil	Prussia, 1907 Württemberg, Imperial Territory, 1912	40 to 60	7 to 10	900 to 940	− 5
	Bavaria, 1907	50 to 80	7.5 to 11	905 to 940	− 5
	Baden, 1910	25 to 60	6 to 10	900 to 950	− 5
	Saxony, 1910	40 to 60	6.5 to 10		− 5
Winter oil	Prussia, 1907 Württemberg, Imperial Territory, 1912	25 to 45	4.5 to 7.5	900 to 940	− 20*
	Bavaria, 1907	25 to 50	4.5 to 7.5	905 to 940	− 15*
	Baden, 1910	25 to 60	6 to 10	900 to 950	− 12
	Saxony, 1910	25 to 45	4 to 7	....	− 20

52

FOR RAILWAY CAR LUBRICATION

Acid value calculated as per cent oleic acid not more than	Flash point, °C.		Remarks
	Pensky-Martens	Open vessel	
2 12		160	Not more than 0 2 per cent insoluble in "normal benzine."
2 12	145		Not more than 0 3 per cent insoluble in "normal benzine."
0 19		150*	* Burning point over 190°; not more than 0 5 per cent insoluble in "normal benzine," not more than 6 per cent boiling under 300°, not more than 13 per cent residue on distillation.
0 00			..
2 12		145	Not more than 0 2 per cent insoluble in "normal benzine." * Sample heated to 50° before the experiment.
2 12	135	.	Not more than 0 3 per cent insoluble in "normal benzine." * After repeated cooling.
0 19		150	Same remarks as above for summer oil.
0 00	... ...	...	....

PROPERTIES OF STEAM-

		Amount of fatty oil allowed	Engler viscosity at 50°	Engler viscosity at 100°	Specific gravity at 15° × 1000
G. Steam-cylinder oils	Royal Powder Works, Spandau, 1911	0	....	At least 4	. ... . .
	Prussian Railways, 1909	5		Same	Not under 885 at 20°
	Bavarian Railways, 1910	0	.	At least 3*	890 to 950
	Wurttemberg Railways, 1909	5	. . .	At least 4*	890 to 950
	Baden Railways, 1910	0	At least 30	At least 3	890 to 940
	Prussian Military Railways	0		About 4	885 to 900
	Imperial Territory, 1912	7 5	. .	At least 4	893 to 923
	....	.. . .	25 to 40	3 5 to 5	
H. Super-heated-steam cylinder oils	Royal Powder Works, Spandau, 1911	0	. . .	At least 4	. .
	Zabrze Mines	5	... ...	7 2	906
	Prussian Railways, 1910	0	....	At least 6 7	At least 900 at 20°
	....	0 to 10	45 to 60	5 to 8 at times to 10	. ..
	Bavarian Railways, 1910	0	. . . .	5 to 7*	890 to 950
	Württemberg Railways, 1909	5	At least 60	At least 7*	890 to 950

Flash point °C.		Amount volatilized in 2 hours, per cent	Acid value calculated as oleic acid per cent, not more than	Ash	Remarks
Pensky-Martens	Open vessel				
260			0 07		For use with steam at 11 atmospheres.
265		Not more than 0 2 at 200°	0 70		
250	280	Not more than 0 1 at 200°	0 35		* Viscosity at 150° over 1 5, soluble in " normal benzine " to clear liquid, not more than 1.5 per cent of asphalt insoluble in alcohol-ether.
265	280	Not more than 0 2 at 200°	0 49	Must be absent	Soluble clear in " normal benzine"; not more than 1 per cent of alcohol-ether insoluble asphalt. * Viscosity at 150° not less than 1.5.
	270		0 11		Liquid at +15, soluble clear in " normal benzine."
290 to 300			0 21		Liquid at room temperature.
275		Not over 0.2 at 200°	0 21		Mixture of 92 5 per cent refined mineral oil and 7.5 per cent of tallow.
250				Less than 0 1	General experience [Schwarz, Mitteilungen, **27**, 19 (1909)].
285		.	0 07		..
300	.	.	0 07		Not more than 0 4 per cent of asphalt insoluble in naphtha.
300			0 7		Not more than 0.2 per cent of asphalt insoluble in " normal benzine." Viscosity at 180° over 1.6.
Near 300 or over				Less than 0 1	General experience (Schwarz, see above).
300	320	After 6 hours at 300° not more than 0.3	.		No residue with "normal benzine"; not more than 1 per cent of asphalt insoluble in alcohol-ether. * Viscosity at least 1.5 at 180°.
300	334**	At 350° not more than 9.2	0 49	Must be absent	* Viscosity at least 1.6 at 180°. ** Burning point above 378°.

XXIX. Formation of Residues

There have been repeatedly found in steam engine cylinders, in cylinders of gas engines, of compressors, and elsewhere, hard, pitch-like, carbonaceous residues* containing softer enclosed materials; these residues were in some cases found after explosions or after disturbances in the working of the machines. The formation of such bodies, which may be caused by many things, is to be traced to the oxidation of the oils; they are generally observed in machines driven by compressed air or superheated steam. The residues consist of lubricating oils, in part unchanged and in part changed to asphaltic and carbonized bodies, besides inorganic materials. In the cylinders of blast furnace gas-engines were found residues containing tar coming from the gases used; in other cases were found bodies containing blast furnace slag-dust, besides oxidized and carbonized lubricating oil. The causes of the formation of these residues are to be looked for in the methods of operation; in no case was the formation of the residues found to be due to impurities or abnormal composition of the lubricating oil used. It is true however that lubricating oil containing about 0.6 per cent of free organic acid has caused residues to form in motor cylinders by the production of iron soaps. And during the war the use, in Germany, of unrefined cylinder oils (containing material insoluble in naphtha) caused much trouble, in operation of motors, and in producing residues.

Allen makes mention of the presence of mechanical impurities, especially sand, which causes wear of the metal surfaces, poor lubrication and local overheating, bringing with it decomposition of the oils. Stolzenberg† tries to find the cause of the formation of these residues from the standpoint of the engineer; he inclines to the view that flue dust, solid particles from the boiler water and iron oxide from the walls of the superheater get into the cylinders with the air or steam and make lubrication doubtful. Certainly in such cases the lubricating oil, in so far as it fulfills its normal functions, is to be considered as a secondary factor in the formation of such residues.

The conditions are somewhat different in the case of Diesel engines run with special fuel oils; in such cases the demands made on the lubricating oils are different from those made on a steam-cylinder oil.‡ During the explosions in these motors, the temperature rises to 1000° and

* Holde, Mitteilungen, **22,** 175 (1904); Chem. Umschau, **12,** 137, 187 (1905); Schlüter, Chem. Ztg., **37,** 222 (1913).

† Chem. Rev., **12,** 137, 187 (1905); **13,** 54, 79 (1906).

‡ Schlüter, Chem. Ztg., **37,** 222 (1913).

a part of the lubricating oil, which is not cooled by the walls of the cylinder, is burned. If the oil is asphaltic, the burning may be incomplete, carbonaceous residues resulting; since fatty oils frequently do not burn completely, for motor cylinder lubrication there should be used light-colored mineral oils of viscosity 4 to 11 at 50° and free from asphalt, acid and fat.

In the examination of such residues, they are first extracted with chloroform; after removing iron splinters with a magnet, the insoluble matter is treated with hydrochloric acid, whereby iron, iron oxide and iron soaps pass into solution in which they may be detected by the usual procedures of qualitative analysis; the portion insoluble in chloroform and also in the acid generally consists of carbon, sand and gangue, the carbon being determined by ashing. After evaporating the chloroform an oil can be extracted from the residue by means of low-boiling naphtha; this oil in specific gravity and elementary composition is usually very much like the lubricating oil used, while that portion insoluble in naphtha but soluble in chloroform, is easily soluble in benzol and is recognized as asphalt.

In the following, the results of several investigations of residues are given.*

TABLE 54

Elementary Analyses of the Oil and the Residue

	Per cent of					
	Carbon	Average	Hydrogen	Average	Oxygen by difference, average	Ash
Original oil	83 7 83.6	**83.7**	12.0 11.9	**12.0**	4.3	....
Portion of the residue soluble in naphtha	(81.8) 83 6	**(82.7)** **83.6**	11 5 11.7	**11.6**	5.7	0.3
Portion of the residue insoluble in naphtha, soluble in benzol	83.5 83 4	**83.5**	11.5 11.6	**11.6**	4.9	....

Case 1. This residue (Table 54) was found in an air compressor. It was made up of hard and soft parts and had an odor of carbonized matter. The original

* In one case where a rape oil was used instead of mineral oil in lubricating a mine drill, a violent explosion took place and two workmen were overcome, one fatally, by the resulting gases (CO and CO_2); it was shown that the cause of death was CO (Ztsch. f. d. Berg., Hütten-u. Salinenwesen, **1900,** 178). According to the investigations of Engler (Ber., **1889,** 592) the possibility of the formation of CO from fats is recognized.

mineral oil was grey green, red by transmitted light, and contained beside pure mineral oil traces of neat's-foot oil, and had a flash (Pensky) point of 253° and an acid value of 0.

Of the residue 35 per cent dissolved in naphtha boiling under 50°, a further 3 per cent in benzol, this portion being brownish black, viscous and having a faint odor. The insoluble part was brown black when rubbed, having the appearance of asphalt; it contained iron oxide and carbon. Traces of sulphur were found in the oil and in the soluble part of the residue; nitrogen was absent. This residue, like the other one, resulted from decomposition and oxidation of the original oil.

Case 2. This residue was a brown-black granular mass. The ash in the superheated steam cylinder oil amounted to 0.008 per cent. The residue contained 27 per cent of material soluble in chloroform of which 25 per cent was viscous dark mineral oil and 2 per cent was asphalt insoluble in naphtha. The 73 per cent insoluble in chloroform consisted of: 44 per cent of carbon-like organic bodies, 7 per cent iron oxides 9 per cent of inorganic material insoluble in hydrochloric acid, mainly sand (silicon dioxide), 2 per cent of alumina, 2 per cent of lead oxide, 6 per cent of lime, 2 per cent of magnesia and 1 per cent sulphur trioxide, united with lime.

The large amount of inorganic material indicates that the oil was not the cause of the deposit. The grains of sand found suggest an accidental impurity, leading to friction and local overheating. From the presence of asphaltic material and iron oxide, prolonged disturbance might be assumed. A guess might suppose that grains of moulding sand, or similar material, had not been completely blown out of the castings during the assembly of the machine.

XXX. Condenser Water

If the condensed steam from a steam engine is to be used again as boiler water, this water must first be freed by filtration from entrained lubricating oil. The question often arises whether such filtering installations are working well; that is, it is necessary to determine if the filtered water is sufficiently free from oil, or if there is danger of the oil attacking the walls of the boiler.

The oil is extracted from 1 to 2 liters of condenser water by means of freshly distilled ether (the apparatus must all be washed free from oil and the cock of the separatory funnel should not be greased); the water is extracted with successive 100 c.c. portions of ether until the last treatment leaves no residue on evaporation. The united extracts are filtered, distilled and the residue dried for 5 minutes at 105°. The cooled oil is to be examined for acidity and other properties which might be of importance in estimating its corrosive action on the walls of the boiler.

Zschimmer* suggests that the oil may be precipitated by forming a fine flocculent precipitate of iron hydroxide or aluminum hydroxide in which the oil is enclosed and from which it can then be extracted. This is especially suited for concentrating the oil in a water containing very little.

For the purpose, 3 to 5 liters of water are used, a precipitate of aluminum hydroxide is formed from alum and sodium carbonate, and this precipitate is extracted

* Petroleum, **5,** 419 (1919); Chem. Zeitung, **41,** 543 (1917).

with ether. Ellis* explains this action by assuming that a negative charge is carried by the colloidal oil particles which are attracted to and precipitated by the oppositely charged particles of iron or aluminum hydroxide.

K. Conducting Lubricants

The mineral oils used as transformer oils, because of their insulating power, may be made conducting† by dissolving in them alkaline earth and heavy metal salts of naphthenic acids. Not many uses have been found for such materials. Street railway trolley wheels are lubricated‡ with electrically conducting paste containing graphite. Sliding contacts are lubricated and made conducting by the use of Acheson-graphite paste. Magnesium oleate, alcohol, and acetic acid may be used to make naphtha conducting (see page 122).

G. Jaffe states that the specific conductance of ideally pure petroleum ether rises on the addition of 0.8 milligram of lead oleate from less than 10^{-18}, to about 10^{-13} or 10^{-15}. Holde tested the conductance of certain oils by the galvanometer method already described (page 65).

Pure, pale mineral lubricating oil at 18° had a specific conductance of at most 10^{-13}; the addition of 7.5 per cent of naphthenic acid changed this to perhaps 7×10^{-12}, but the equivalent amount of calcium soaps gave a value 6.6×10^{-10}. The soap is more ionized than the acid itself.

A dark viscous petroleum residue (fuel oil), containing 1.7 per cent of naphthenic acids (calculated as oleic acid) had a specific conductance at 18° of 5.8×10^{-11}; after removal of the acid, it was 3.3×10^{-11}; the conductance was not much altered by this removal. The conductance of the material free from acids, but still containing oxygen and sulphur derivatives asphaltic in nature, was however 100 times that of the pure machine oil distillate mentioned above.

An anthracene oil (pressed from anthracene) containing 1.5 per cent of creosote had at 18° a specific conductance of 4.7×10^{-6}; after treatment with potash solution, it dropped to 4.5×10^{-9}, after again treating, it dropped to 3.5×10^{-9}. The tar oil seems to have a considerable conductance; but it may be possible by an electrical convection to rid such oil of conducting material (see page 64).

The calcium salts (and other alkaline earth and heavy metal salts) of naphthenic acids may be mixed (up to 30 per cent) with heavy min-

* J. Soc. Chem. Ind., **29**, (1909).

† Berichte, **48**, 14, 288 (1915).

‡ Dierbach, Ding. Poly. Jour., **95**, Bd. 329, Heft 21/22 (1914).

eral oils, the viscosity being much increased. Such oils are useful as gun oils,* since the soaps present neutralize the nitric fumes produced by smokeless powders, thus protecting the gun barrels against corrosion.

L. Lubricating Greases

I. General

The lubricating greases used for economy or for the lubrication of difficultly accessible parts of machinery consist of a solution of calcium or magnesium soap (or mixtures of these with sodium soap) in heavy mineral oils, with the addition of a little water (0.5 to 7 per cent); they may also contain small amounts of unsaponified fatty oil, separated glycerine, free lime, coloring matter, deodorants, and substances to cover the fluorescence.

In Germany before the war, rape oil, tallow, and similar materials were used as raw material for the soap, and heavy mineral oils were considered necessary, but because of the scarcity of such material, sodium soaps of montan-wax acids and mineral machine oils of low viscosity ($E = 2.5$) were used during the war.

These greases are usually prepared† by dissolving the fat (or montan wax) in a small amount of mineral oil, saponifying with caustic lime or caustic soda in a kettle heated to 110° by steam coils, and then adding the major portion of the mineral oil. The mixture is allowed to cool while stirring, is then run through rollers while lukewarm and kneaded to a salve-like consistency.

For wagon greases, lignite tar oils or rosin oils may be used instead of mineral oil, and barytes or talc are added as loading materials. Resins and montan wax are used to make the soap. Such greases have been found useful where pressure and velocity are low.

The composition greases may be considered as water emulsions of colloidal solutions of soap in mineral oil. The water is distributed through the grease in infinitesimal drops of high surface tension and gives to the greases their peculiar consistency and high dripping point (75 to 85°). If the grease is heated to the dripping point, the water droplets will disintegrate, the salve-like nature of the grease disappears and the grease may become transparent, and oil may separate. Grease made by dissolving calcium soap in mineral oil in the absence of water will soon lose its homogeneity.

* D. R. P. 261070.

† See Holde, Ztschr. f. angew. Chem., **21**, 41, 2138 (1908); Ztsch. f. Ind. d. Koll., **1908**, 6. Also Jour. Ind. and Eng. Chem., **1**, 357 (1909).

Besides the greases mentioned there must be considered those of a consistency like that of butter or tallow, used for ships-engines, these consisting of alkali soaps and completely saponifiable substances, the grease being easily emulsified with water; cable-coating or wire rope grease for protecting cables from wear and corrosion, containing solid fats, wax, oil, talc; a similar material used as chain grease for cranes, hoists, etc.; hot neck greases for lubricating parts subjected to high temperatures, some of these being mixtures of fat pitches and petroleum pitch, some containing saponified wool grease, or other waste fats to which has been added rosin or rosin oil; harder vaseline briquets consisting of mineral oil and sodium soap, used in the lubrication of rolls in steel mills. Gear grease consists of the usual grease to which has been added graphite or talc and tar; rosin, wax, paraffin and ceresine are sometimes added.

II. Examination

A general method of procedure is hard to find; because of the great difference in composition and the great variety of uses to which they are put, widely different methods of analysis may be used.

In the typical consistent fats or greases the following points must be considered:

(*a*) **The External Appearance** is of importance. The grease should be well mixed and uniform in composition; no granular particles of soap or lime must be present. Additions like rosin oil, tar oil, nitrobenzol, etc., can be detected by their odors. A light yellow, brown or red color is preferred.

(*b*) **Dripping Point.** For determination, see page 37.

The dripping point is dependent on the amount of soap and of oil contained in the fat, the amount of water, the temperature and length of heating on dissolving the soap in the oil, whether the soap was made by boiling or precipitation, the intimacy of contact of the water and the oil-soap solution, the viscosity of the mineral oil used and the fat used for making the soap.

Some greases differ (according to Holde) more in the temperature of flow than in the dripping temperature. The temperature of flowing should always be observed, it generally being 5° below the dripping temperature; with very soft, and also with very hard greases, differences of 50° have been observed. The temperature of flowing, however, rises considerably on storage. The dripping point of greases generally lies between 75° and 83°; with greases for rolling mill use, it may, however, be as high as 130°.

(*c*) **Kissling's Method for Determining the Consistence of Fats.** The following apparatus has been constructed for determining the consistence of greases which do not flow from the Engler viscosimeter (Fig. 105). In this is measured the time necessary for a pointed cylindrical rod to penetrate a definite distance into the grease.

An aluminum rod A, 300 mm. total length and 9 mm. thick, has a pointed end 55 mm. long; it carries at the top a circular brass plate ab with pointer s underneath, 10 mm. long. Above the plate is a 40 mm. long rod t which is to hold the weights of 25, 50, 100 and 200 grams. The distance from the end of s above the horn ring r should be 100 mm. The fat or grease is filled into the beaker to a height of 125 mm. at 20°, the point of the rod being put on the surface. After releasing, the exact time necessary for the pointer s to drop to the ring 100 mm. away is determined. The load is to be so chosen that the time of sinking is not less than 20 or more than 100 seconds. The empirical calculation of the consistence is made by adding two quantities, one of which is a fraction of the weight of the rod plus load and the other a fraction of the time of sinking expressed in seconds. In this way Kissling arranged the fats and greases examined in 9 classes of consistence, the calculation of which follows according to Table 45. The consistence K is

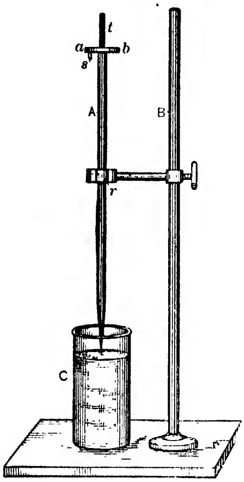


FIG. 105.

$$K = \frac{b + s}{10},$$

where $b = \frac{p}{2}$, p is the weight of the rod; $s = \frac{t}{d} = \frac{\text{time in seconds}}{\text{divisor}}$. Regarding the size of the divisor see Table 55. For many purposes this method gives results sufficiently close; the difficulty lies in filling the fat into the vessel evenly, single hard particles causing a decided error.

TABLE 55

Degree of Consistence	I	II	III	IV	V	VI	VII	VIII	IX
Weight of rod in grams	50	50	50	50	50	50	50	50	50
Weight added . .	. . .	25	50	100	150	200	250	300	350
Total weight (p).....	50	75	100	150	200	250	300	350	400
$b = \frac{p}{2}$.............	25	38	50	75	100	125	150	175	200
Divisor (d) of the time of sinking (t)	20	10	5	4	3	2	1.5	1	1
Consistence observed	under 3	3 to 5	4 to 7	7 to 10	10 to 13	13 to 17	17 to 22	22 to 28	over 28

(*d*) **Preliminary Qualitative Tests.** If the grease dissolves clear in naphtha or ether, which is rarely the case, and if it leaves no ash on a platinum foil, then no added soap or inorganic loading material is present. If the grease is completely soluble in naphtha, the grease is examined in the usual manner see page 75. If the grease is partially insoluble in naphtha, as is the case with wagon and machinery greases, a sample is treated under a reflux condenser with 90 volumes of naphtha and 10 volumes of absolute alcohol, allowed to stand for some time and then filtered while hot. Fat, soap and mineral oil are dissolved, while free lime, calcium carbonate and additions such as barytes, diatomaceous earth, graphite, etc., are found in the residue and are examined in the customary manner.

The high-melting greases are difficultly soluble in alcohol-naphtha (1 : 9) because they contain alkali soaps; in such a case, an alcohol-naphtha (2 : 8) mixture is used (and if necessary more alcohol is added).

A preliminary test for free acid or free lime is made by heating the grease with 80 per cent alcohol (slightly alkaline, or neutral) containing phenolphthalein. Generally the neutral solution turns red, since, as a rule, a slight excess of alkali is present in the grease; in such a case the test for free acid is unnecessary.

(*e*) **Quantitative Determination.** 1. **Free Fatty Acid.** This test is generally unnecessary, since the greases, if they do not contain a considerable excess of fatty oil, contain the fatty acid only as soap. Marcusson advises that the following method be used, if a determination is necessary:

10 grams of grease are heated for a short time under a reflux condenser with a neutralized mixture of 90 volumes naphtha (sp. gr. 0 70) and 10 volumes of absolute alcohol. Greases not artificially loaded dissolve completely or nearly so; the undissolved matter is filtered off and washed. After adding 30 c.c. of neutralized alcohol (50 per cent), the filtrate is titrated (shaking and warming) with $N/10$ alcoholic sodium hydroxide in the presence of phenolphthalein, until the lower alcoholic layer remains rose colored. The two layers separate very easily while hot.

The use of diluted alcohol in the test is important; when 96 per cent alcohol is used in the presence of naphtha or ether, as is the case with light-colored lubricating oils, the color change is often inexact and unsatisfactory. The sodium hydroxide besides neutralizing the free acid also decomposes the calcium soaps; the resulting basic substances (calcium hydroxide or basic soap) allow a sharp color change to take place only in the presence of water.

The above method can be used only when no other substances which might react with the alkali are present. For example with a grease used for soldering

and containing zinc chloride, the sodium hydroxide would form zinc hydroxide or soluble zincate, thus interfering with the titration of the acid. In such a case the zinc chloride should be first extracted with water, the grease being dissolved in naphtha and alcohol. A preliminary test for basic radicals is recommended.

2. **Soap.** The method is the same as that described on page 195 with the following changes.

(α) **Volumetric Method of Holde.** 10 grams of fat, 50 c.c. of naphtha and 10 to 15 c.c. of dilute hydrochloric acid are boiled in a 300 c.c. flask under a reflux condenser; the liquid is washed into a separatory funnel with naphtha and the acid layer is run off, caught separately and the nature of the soap base (generally calcium) is determined qualitatively. Often the hydrochloric acid layer appears red because of the coloring matter added to the grease; in that case the fat is repeatedly treated with acid till a colorless extract is obtained. With uncolored greases, two extractions of the naphtha layer with hydrochloric acid suffice. The mineral acid is removed by washing with Glauber's salt solution; the naphtha solution is then washed twice with distilled water and titrated with $N/10$ sodium hydroxide, after adding 20 c.c. of neutralized alcohol and some phenolphthalein. The acid value thus determined represents the sum of the free and combined (as soap) acids. After subtracting that due to free acid as determined above, the acid combined as soap is obtained. To calculate the amount of soap, the molecular weight of the acids and the nature of the basic radical must be known.

To determine the molecular weight the titrated naphtha solution (of the grease split with acid) is diluted with enough water to make it 50 per cent alcoholic, taking account of the 20 c.c. of absolute alcohol added and the amount of 96 per cent potash used. It is well to avoid emulsion by adding a few c.c. of strong aqueous KOH and the same amount of absolute alcohol. The naphtha solution is several times shaken with 50 per cent alcohol according to Spitz and Hönig, running off the lower aqueous layer. From the alcoholic soap solution (purified by repeated shaking with boiling naphtha) the fatty acids are separated as per page 198. To determine the molecular weight of the acids, ½ to 1 gram is dissolved in neutral absolute alcohol and titrated with $N/10$ KOH; from the acid value thus obtained, the molecular weight is calculated as follows:

$$M = \frac{56110}{\text{acid value}}.$$

The calculation of the amount of soap is made as by formula of page 195.

(β) **Gravimetric Method of Marcusson.*** This depends on the slight solubility of soaps in acetone and easy solubility of mineral oils in this solvent. However certain soaps (such as rosin soaps) are considerably soluble in acetone, and viscous mineral oils, also wool fat, are not completely soluble in cold acetone. The following method must therefore be used with caution.

A weighed amount of grease is extracted in a Soxhlet apparatus with acetone containing granular calcium chloride. The latter unites with water and lessens the solubility of the soaps. The insoluble portion, which may still contain mineral

* Laboratoriumsbuch, 133; Chem. Umschau, **20,** 43 (1913).

oil, is extracted with a mixture of 3 parts acetone and 1 part low-boiling naphtha. The residue contains the soap and inorganic bodies (lime, loading materials, graphite); the soap is separated by solution in naphtha-alcohol (8 : 2) mixture.

3. **Unsaponifiable Matter and Unsaponified Fat and Oil. (Neutral Fat and Mineral Oil.)** From the naphtha solution obtained according to 2 α and freed from soap, the solvent is distilled, the residue (neutral fat plus mineral oil) weighed. By determining the saponification value of the residue, the amount of saponifiable fat can be estimated (see page 195) and calculated to the original amount of grease.

If the properties of the mineral oil free from fat are to be determined, the mineral oil must be separated by the method of Spitz and Hönig (page 197) and tested for foreign matter (according to page 198), Engler viscosity (page 16) and its solidification temperature (page 36). There may be as much as 75 to 80 per cent of mineral oil in greases.

4. **Total Fat.** 10 grams of sample are boiled under a reflux condenser with 100 c.c. of ether and an excess of dilute HCl (10 c.c.) till clear. After decantation and complete extraction of the acid layer, the combined ether extracts are washed with Glauber's salt solution and then twice with distilled water to get rid of mineral acid. The ether is evaporated and the residue dried at 105°. This consists of the total fat (mineral oil, neutral fat and fatty acids set free from the soaps).

5. **Moisture** is determined according to the method of page 72.

6. **Glycerine.** This is present in greases only by accident and in small amounts, being formed during the saponification of the fat added. It is determined only in exceptional cases. Qualitatively it is determined* by oxidation to glycerose by hypochlorite and reaction of the latter with orcin. It is determined quantitatively by the acetin method in which is used the acid liquid obtained by decomposition of 10 grams of grease with naphtha and dilute HCl. After clarifying, pouring through a double filter and washing, the filtrate is treated as on page 455.

7. **Free Lime.** Small amounts of free lime are found in greases, they being introduced during the preparation of the grease. A preliminary test is made by shaking several grams of fat with a 40 per cent alcohol containing phenolphthalein; the red color is due to calcium hydroxide, rarely to hydroxides of the alkali metals.

10 grams of sample are heated 15 minutes under a reflux condenser with 50 c.c. of naphtha and 5 c.c. of alcohol The undissolved matter is filtered and completely washed out with hot naphtha-alcohol in a hot water funnel. In the residue, free from fat and soap, the calcium hydroxide can be determined in the usual manner.

8. **Added Substances.** Loading materials such as gypsum, barytes, starch, talc, graphite and lampblack remain undissolved in the treatment of 7 and can be identified by the customary qualitative methods.

* Mandel and Neuberg, Bischem, Zeitschrift, **71**, 214 (1915).

9. **Accidental Impurities.** Coloring substances are added only in traces and need not be determined as a rule. The same is true of the determination of nitronaphthalene which is added to cover the bloom of the mineral oil added; if necessary it can be qualitatively and quantitatively determined according to page 75.

TABLE 56

SPECIFICATIONS OF THE GREATER BERLIN STREET RAILWAYS FOR LUBRICATING GREASES

	Melting point, °C.	Soap content, per cent	Moisture, per cent
Grease	90	22 to 25	up to 4
Axle grease	85	18 to 20	up to 4
Gear wheel grease	60 to 65	up to 15	

Specifications of the Imperial Wharves, Wilhelmshaven

The machinery grease must have been made from pure mineral oil by the addition of the vegetable oils necessary for saponification. The amount of vegetable oils must not exceed 20 per cent. It should be free from acid and should be homogeneous and of a lard-like consistence. Non-fatty or non-soapy parts, except for the water necessary, and glycerine, should not be present. On standing, soap should not separate and no changes of oxidation or evaporation should take place.

Specifications of the Royal Powder Works at Spandau

The solid machinery grease should consist of calcium soap, mineral oil and water, and must be well purified and free from foreign substances. Organic acids, calculated as oleic acid, should not exceed 2.12. The grease should change its solid consistence little between − 5° and 25° and should always have a uniform lubricating power. It must not resinify on longer standing in air. Heated 10 hours to 100°, the grease should not be resinous or dried up after cooling. Flash point (Pensky) should not be under 150°.

Specifications of a Mining Company for Rope Grease

The rope grease must be free from tar, acid and tar oils, must not contain more than 2 per cent of inorganic components and should not resinify or crumble in use. It should have a salve-like consistence, be easily applied with a brush and must not change on standing or in use. In winter it should be supplied in liquid form and guaranteed not to freeze, while in summer it should be solid.

M. Graphite Lubrication

I. General

Graphite has been used for many years* for reducing the temper-

* Petroleum, **7,** 939 (1912); **8,** 681 (1912). Ding. Poly. Jour., **94,** 257 (1913). Z. Elektrochemie, **23,** 116, 120, 121, 181 (1913). Chem. Ztg., **40,** 358 (1916). Chem. Ztg. Rep., **56,** (1897). See also Seifensiederztg., **40,** 1198, 1239, 1384, 1418, 1446 (1913); **41,** 146 (1914).

atures of hot-running bearings; it has also been found useful in preliminary runs with new machinery. Engineers have gradually adopted the use of graphite for producing a better bearing surface and supposedly to decrease the amount of oil used, it being assumed that a decrease in the friction because of better bearing surface would mean a smaller oil consumption. Thurston has published important work on the value of graphite in lubrication.

During the war Germany was unable to get supplies of mineral lubricating oils from the United States or Russia. The German Bureau of Commerce and Industry therefore issued a bulletin concerning the use of graphite, as follows: —

The value of graphite in increasing the lubricating value of an oil is well known. But graphite should be used only if it is free from hard mineral components. It should itself be in a finely divided scaly condition. It will not attack the bearing under these conditions, in fact it will coat itself over the surface of the metal, filling up inequalities and depressions. Because of the scaly nature, it is not easily squeezed out from the bearing, in fact keeps the surfaces separated sufficiently to allow the penetration of oil. The action is an indirect one; for that reason, the action of graphite will be less noticeable with bearings under slight pressure.

In using graphite, the reservoir for the lubricant must be located in some elevated position, so that the oil need not ascend at any point, otherwise stoppages in feed will occur. A too rapid supply of graphite must be avoided, since it is likely to collect in certain places, as in steam cylinders, in deposits or balls which may cause damage; as a rule small additions of graphite are sufficient.

When dry graphite is mixed with oil, it is likely to settle in the oil reservoirs and cause stoppages in the passages of the oil tubes. A stirring device must be provided if such graphite is to be used; this may cause a reduction of fifty per cent in the amount of oil necessary. Stirring apparatus is recommended only with larger machines.

Such stirring devices are unnecessary if graphite is provided in a condition which may be described as colloidal. In this condition, it will not sediment to any important degree. Such preparations may be tested by allowing the sample to stand for some weeks. A bit of filter paper is then dipped for several millimeters into the liquid. If the paper appears black, the mixture is satisfactory. A layer of clear oil on the surface should not be present.

The graphite-oil mixture should be added in amounts ranging from 0.5 to 2 per cent. If a poor grade of graphite-oil mixture is used in too large an amount, a separation of graphite may take place; this leads to stoppages. In various tests 0.5 per cent of the graphite-oil mixture was found most satisfactory.

A saving of oil has resulted whenever graphite-oil mixtures were used; in some cases this has exceeded 50 per cent. The preparations are expensive, but only small amounts need be used, and the saving in oil is considerable. The graphite is easily precipitated in oils containing acidic materials; its use is not recommended for use with such impure oils. Graphite-oil mixtures produce precipitates on contact with water; these may cause trouble. Where water is likely to come in contact with the bearings, it is well to inspect them frequently.

Graphite has been found very useful when applied in the form of a compound grease. A separation does not take place here, so ordinary graphite can be used. A mixture containing 25 per cent of graphite, caused a 50 per cent saving in grease. Smaller amounts are also satisfactory

The above official recommendations have been substantiated by the experience of large industrial concerns.

The graphite used should be free from mineral material which may have an abrasive action. Graphite may contain as much as 70 per cent of mineral matter, of which some may be quartz particles with sharp edges. The use of such material invariably causes an abnormal wearing down of the bearing surfaces.

A natural graphite which caused such abrasion was found to contain 10.9 per cent of ash; in this were present a considerable number of angular, coarse quartz particles of 0.1 mm. diameter. On the other hand another graphite (containing 14.2 per cent of ash, but little quartz and only amorphous particles of 0.03 mm. diameter) was found to improve, and smooth out the surfaces of a bearing which had been roughened with a file. Some handbooks and instruction books advise the use of graphite which is free from ash; this is probably an extreme point of view.

Certain ash components do not seem to be harmful. The kind of bearing surface must also be considered. Graphite, with considerable ash and containing quartz particles, when well stirred into steam cylinder oil by mechanical devices has been found in some actual cases to cause no disturbances in operation or damage to the cast iron cylinder walls, but has actually been found to effect a considerable saving in oil. But additions of such material are not in general recommended.

It sometimes happens that disturbances will arise in the use of certain bearings with oil lubrication through the accidental entrance of sandy particles, dust, etc. into the bearings, causing friction and heating. The addition of graphite improves the working of such bearing and helps to smooth out unevenness in the bearing surfaces, and by reduction of friction produces a more economical use of oil.

Graphite is added to decrease friction; but if the graphite separates in the oil tubes, it may lead to increased friction, and to heating; the prevention of such clogging of the supply of lubricant is important.

The precipitation of the graphite in the lubricating canals with different types of oilers can be prevented by proper design of the supply system, by the use of sufficiently pure graphite (best in colloidal suspension), by the use of stirring devices when non-colloidal graphite is used, and by avoidance of an excess of graphite.

It has happened that where carefully adjusted bearings and journals have been lubricated with oil, the addition of graphite has produced an increase in the friction (of only a few per cent however). This may happen where the mounting of the machine has been exceptionally well done. With the greater proportion of lubricated bearings, however, the adjustment of bearing and journal is only approximate. In such cases the use of graphite and oil has been of advantage from the frictional standpoint, as well as more economical in the use of oil. In some cases it has been advantageous to entirely dispense with the use of oil and substitute a graphite-grease; even though this did somewhat increase the friction, it was economical from the standpoint of lubrication.

Acheson was able to prepare an artificial graphite in an electric furnace by transformation of the carbon of anthracite coal. By grinding, and subsequent treatment with ammonia and gallo-tannic acid in the presence of water, he obtained a colloidal solution of the graphite (hydrosol) which he called "aquadag." By intimate mixing with oil, or by evaporation of the water under definite conditions in the presence of oil, he was able to transfer the graphite to the oil, producing "oildag" "Oildag" contains from 10 to 15 per cent of graphite and must be mixed with from 50 to 200 volumes of lubricating oil for actual use.

Natural graphite has also been converted* into products similar to "oildag" and "water dag." The graphite is freed from mineral matter by treatment with concentrated sulphuric acid and hydrofluoric acid; it is then treated with sulphuric acid and permanganate or chromic acid, washed with water, and after removal of electrolytes changed into a stable suspension by the addition of a protective colloid. The graphite can be precipitated from this suspension in such a condition that it will redissolve on treatment with oil. Such water and oil suspensions of natural graphite are now being manufactured industrially.

Freundlich† has found the major portion of "oildag" particles to be of ultramicroscopic size (smaller than $1\mu = 0.001$ mm.); only a fraction of the particles have a size ranging from 1μ to 6μ. At 1200 magnifications the graphite particles did not appear spherical, but seemed scaly. Practically all samples of natural graphite suspended in oil gave on long standing an upper layer of clear oil. As a rule, however, the dilution of graphite-oil mixture accelerates the

* Karplus, 1913. D. R. P. 292, 729 and 293, 848.

† Chem. Ztg., **40,** 358 (1916); Physikal. Zeitchr. **1916,** 124.

coagulation of the graphite more than does the size of particles; and the effect of dilution is not the same for all oils.

The suspended natural graphite is being used in many industries. It is well to keep in mind in choosing a diluting lubricating oil that the graphite particles settle less rapidly in the more viscous oils. The presence of small amounts of fatty acids or naphthenic acids does not seem to have the coagulating effect on the graphite that is ordinarily expected; this may be due to the slight dissociation in oil of these components, and therefore relatively insignificant action of these as electrolytes.

Thurston, Mabery, Benjamin and Saytzeff have carried out experimental studies on the effect of " oildag " additions on lubricating power. Their experiments with oil-testing machines have demonstrated the oil-sparing and friction-reducing ability of graphite additions. It is probably true, however, that in the field of liquid friction, as with well constructed ring oilers which supply a liberal amount of oil, the graphite has very little influence. With semi-liquid and dry lubrication as with heavily loaded and slow moving journals (possibly over-heated bearings) the influence of the graphite is markedly beneficial. The cooling effect of graphite may be partly connected with its heat conduction. The conduction is 0.0117 for graphite; for cylinder oil it is only 0.000290, or about one-fortieth that of the graphite. The surfaces smoothed by graphite require a smaller lubricating layer than the uneven metallic surfaces. This would seem to mean a saving of oil. The adsorptive power of graphite for oil may help in drawing the oil to the bearing surface.

The friction is slightly increased when graphite is added to an oil; this may be in part due to an increase in the viscosity of the oil. For it has been shown that on adding one per cent of " oildag " to a mineral machine oil of Engler degree 11 at 20° C. there was a rise of the viscosity to 11.6; with an oil of $E = 42.8$ at 20° C., the viscosity rose to 44.7. Since the change in viscosity was slight (the addition was larger than is usually considered necessary) one may calculate on a minimal increase in the viscosity on adding graphite. With a very viscous oil, no change in the viscosity was noticed on adding graphite; this oil when used on a testing machine did not show any change in the frictional coefficient on adding graphite.

Industrially graphite has been used for many years. It has been recognized as contributing to the economical use of oil and as an aid to lubrication. On examination of reports concerning unsatisfactory results in the use of graphite it has been found that the trouble might

have been due to an unfamiliarity with the use of graphite or to the use of a poor quality of oil. For it has been shown that cylinder oils (rich in asphaltic material, which would give a large precipitate with naphtha), which in peace times would not have been used for cylinder lubrication, gave, when combined with graphite, considerable deposits in the cylinders. Mobile machine oils when mixed with graphite proved much more satisfactory in service. Various concerns have noted in the use of graphite a small saving in the amount of oil used (about 13 per cent) and have remarked on the excellent condition of journals and bearings, and of cylinder walls after the use of a lubricant containing graphite. The amount of graphite added need not be great, in fact larger amounts may lead to stoppages of oil passages by a sedimentation of the graphite; thus a 0.5 per cent addition of " oildag," equivalent to 0.1 per cent graphite in the oil, produced no precipitate of graphite, but when one or two per cent of oildag was added, graphite deposited, finally preventing the functioning of drop-oilers. This simply goes to show that the suitability or unsuitability of graphite for lubrication depends on many secondary factors which must be considered before a decision can be made.

In using graphite, it is at times advantageous to run the machinery with oil alone, then to run with oil containing graphite, then again with oil alone; it is thought that this may prevent the stoppage of oil passages by washing away with oil any graphite precipitated in the canals, while the frequent applications of graphite exert a slight abrasive action and keep the bearing surfaces smooth.

II. Examination

(a) *Dry Graphite*

The examination consists of a determination of the external appearance, degree of fineness, moisture, ash, carbon content of the scales or powder, and an estimation of the amount of quartz particles in the ash as well as a microscopic study of the ash components.* In less complete analyses, the determination of moisture and carbon-content can be omitted.

The colloidal graphite preparations are usually free from ash, but the ground-up natural material contains amounts of ash varying from 5 to 60 per cent; this may consist of mica, clay, or quartz and according to the amount of iron contained may have a color ranging from grey to brown. Graphite flakes and graphite powder are somewhat different in their properties.

* Scheffer, Tech. Ruudschau d. Berliner Tageblatt, Nr. **32**, 249 (1916).

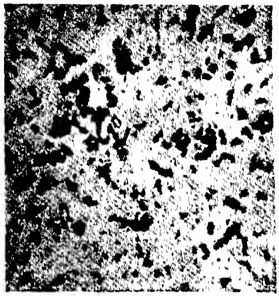


FIG. 106.

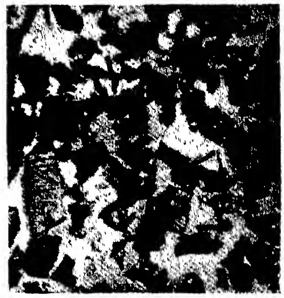


FIG. 107.

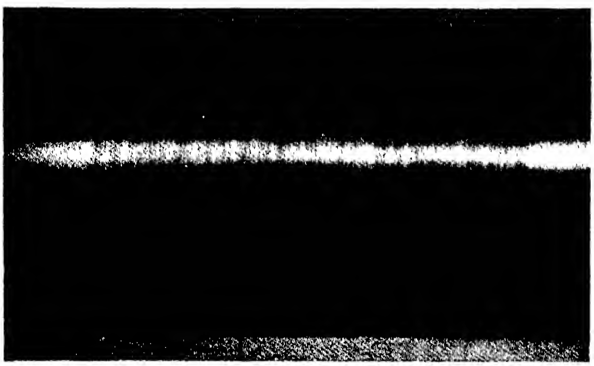


FIG. 108.

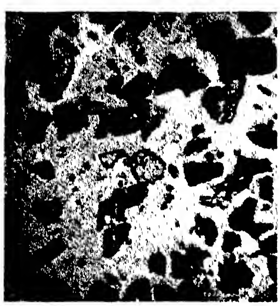


FIG. 109.

FIG. 110.

1. Hygroscopic moisture is determined by heating 1 gram of graphite for 1 hour in a weighed crucible to 105° (in a toluene bath). The loss in weight ranges from 0.08 to 1.53 per cent.

2. **Ash and Quartz.** The dried sample (from 1) is heated in an electric muffle to red heat until constant in weight. The ash thus determined ranged from 4.6 to 66.3 per cent. The quartz is then separated from the rest of the ash by fusion with ammonium pyrosulphate [$(NH_4)_2 S_2O_7$] at 420°, and removal of soluble silicic acid by treatment with an acid mixture containing 50 volumes of HCl (1.06) and 1.5 volumes of concentrated HF. The quartz is not affected by these treatments; it is examined microscopically.

Figure 106 shows a photo-micrograph of a powdered natural graphite (with 14.2 per cent ash and 9.9 per cent of quartz) which when used with oil (1 per cent added) did not abrade the bearings or journal of an oil testing machine; it was even able to smooth off roughness produced in the bearing by filing. Figure 107 shows the larger and sharp-edged quartz particles of a graphite with 10.9 per cent ash, of which 18.3 per cent was quartz; this specimen attacked the soft axle of a ring lubricated bearing as may be plainly seen in Fig. 108. Figure 109 (also 110) shows the coarser but less sharp quartz particles of a steam-cylinder graphite. The graphite of Figure 109 contained 55.2 per cent ash of which 61 per cent was quartz; the graphite of Figure 110 contained 28.2 per cent of ash of which 38.5 per cent was quartz. Both samples of graphite effected a considerable saving of oil. The quartz particles present were in such a condition that no bad effect on the cylinder walls was noticed.

3. Carbon is determined by combustion in a stream of oxygen. The material must be heated in a porcelain tube to redness, as the graphite is difficultly combustible.

The determinations of hygroscopic water and of that obtained by combustion show considerable difference at times; this may indicate the presence of some hydrocarbons or hydrated silicic acid in the graphite.

(b) *Graphite Suspensions in Water or Oil.**

1. Graphite may be used in the form of a colloidal solution or suspension in water (such as "aquadag"). Such solutions are used as boring or cutting liquids in machine shops. Their usefulness depends upon the stability of the suspension of graphite. The amount of graphite is estimated by precipitation with an electrolyte (for example, acetic acid), the graphite being then caught on a filter. To determine whether

* With the assistance of H. Karplus and K. Steinitz. Z. Elektrochem., **23,** 116 (1907). Chem. Zeitung, **40,** 358 (1916). Kolloid Ztschr., **18,** 226 (1916).

the graphite mixed with oil is a mechanical suspension or is in colloidal solution, the following method is used: —

0.25 to 0.5 gram of the sample is dissolved in from 300 to 1000 volumes of benzol, with much shaking; the solution is allowed to stand in a cylinder for 24 to 72 hours; the supernatant liquid is then decanted from the sediment. With colloidal preparations the precipitate will be small in amount and will contain only flaky particles which are easily again suspended in benzol. With preparations free from colloidal particles, the solution above the precipitate will contain very little graphite; the graphite has settled to the bottom as crystalline, scaly, glittering particles.

2. **Stability Test.** The dipping test already mentioned (page 231) is useful in determining the stability of "oildag" samples purchased on the market. It has however been shown that the stability of oil-graphite mixtures depends on the oil with which the more concentrated graphite-oil solution is mixed.

(*a*) **With Light-colored Oils.** 20 c.c. of the oil used in practice are mixed with from 0.1 to 0.3 grams of the graphite preparation by stirring in a porcelain dish. The mixture is allowed to stand in a cylinder; observations are taken from day to day while the cylinder is tilted. Any appearance of separation or formation of a precipitate is noted; if no flocculent material separates in 4 days, the sample is usable. The longer the time before separation begins, the more satisfactory the sample.

(*b*) **With Dark-colored Oils.** The graphite sample is diluted with the oil to be used and allowed to settle in a cylinder. Immediately after starting the test and at the end of 4 weeks, samples are withdrawn from about 1 cm. below the surface and 1 cm. above the bottom. The graphite content of each of these is determined. The smaller the loss on standing, the more stable the oil-suspension of the graphite.

3. **Determination of Graphite.** A Gooch filter is prepared with the asbestos mat covered to a height of 0.5 centimeter with Fuller's earth; its constant weight at 105° is determined. Through the filter (after wetting with benzol) is poured a mixture of 1 gram of sample stirred into 100 c.c. of benzol. The graphite is caught on the filter, while adhering oil is washed off with benzol and finally with carbon tetrachloride or chloroform. By drying at 105°, the weight of graphite in the oil is determined. In some actual analyses this ranged from 8.5 to 18 per cent.

N. Boring, Cutting and Shaping Oils

I. General

It has been customary in the working of metal to cool the surface on which the machine is acting by flooding it with soap solutions, with fatty oil (rape or lard) or mineral oil. The liquids used allow an easier passage of the tools over projections and uneven spots. Pure oil is absolutely necessary for fine and rapid work. But compressed air has been found satisfactory for cooling in many establishments for certain

kinds of work. In cooling brass, water and even milk have been used as cooling liquids. The milk is an emulsion of fat in a colloid.

The cooling oils used usually aid in keeping the cutting edge of the tool sharp but do not cool as readily as do water, aqueous emulsions or soap solutions. For certain work, however, cooling is unnecessary. Emulsions of mineral oil (2 to 5 per cent) in water solutions of ammonium or alkali soaps have been much used; they are prepared by simply mixing the ingredients at room temperature. If made from good material, they attack iron and steel only very slightly.

Instead of using soaps made from fatty acids, other emulsifying materials are now being produced from fatty sulphonic acids (from castor oil), naphthenic sulpho-acids, from the spent lyes of refining oil, and also so-called liquid resins (rosin soaps from the soda lye extract (black liquor) in the manufacture of wood pulp). Recently the heavy oils from pine-tar distillation, which are rich in resins, have been used. Other oils are prepared* in a water-soluble or emulsified form by oxidation of oils and resins by means of air in the presence of alkali.

The oils which dissolve clear in water generally contain, besides mineral or rosin oils, soaps made of various acidic organic materials. The solubility in water has been increased in some cases by the addition of fenchyl alcohol; another method† of increasing the solubility is by adding amyl alcohol or higher alcohols (from so-called liquid waxes) besides alkali salts of fatty or rosin acids.

It is claimed‡ that on treatment of the high boiling petroleum fractions with fuming sulphuric acid at 110°, an oily layer, which is made up of material soluble in water, will form above the acidic tar and the sulpho-acids.

A material similar to the cutting oils has been used for street sprinkling. A heavy crude oil is dissolved in an aqueous solution of ammonium soap; on exposure to the air ammonia evaporates, the oil is left on the street in a little soluble form; it is not easily washed away by rain and therefore it helps to keep down dust.

During the war the Germans used various substitutes for cutting oils which contained no fatty oil and very little mineral oil. Aqueous solutions of cell-pitch (evaporated liquor from the sulphite-pulp process), aqueous glycerine-pitch solutions, solutions of glue and similar substitutes were suggested; usually very little or no mineral oil was used.

* D. R. P. 122451.

† D. R. P. 174906.

‡ D. R. P. 256764.

II. Examination

(a) *Rust-Preventing Power*

Weighed cast-iron, steel or brass plates (30 × 30 × 3 mm.) are placed in glass dishes containing the solution to be investigated; they are removed from week to week, washed with ether and the changes in appearance and weight noted.

(b) *Solidification Point*

The addition of these water-soluble oils to water lowers the freezing point considerably, 80 parts of water with 20 parts of oil giving a solution still liquid at − 5°. This makes such solutions valuable as a substitute for glycerine (as in hydraulic presses). The samples are dissolved in the stated amount of water, and tested according to page 35, allowing to stand from 1 to 4 hours.

(c) *Emulsifiability or Solubility in Water*

Oils containing ammonium soaps are gradually decomposed on exposure to air and their emulsifiability decreases with time. Such oils must be kept in closed containers. Their use is decreasing because of their instability.

Oils containing ammonium soaps on being heated or on treatment with acid lose their emulsifying power.

The stability of solutions of different concentrations (2, 5, or 10 per cent) is observed after standing one or more days in tall cylinders.

(d) *Composition*

(1). **Volatile Materials.** (Water, alcohol, naphtha.) The water is determined by distillation of 20 grams of oil in a liter Erlenmeyer flask with the addition of xylol and pumice (page 72). Clear oils may contain 50 per cent of water. The aqueous distillate is tested for alcohol, after it has been fractionated by redistillation over alkali to hold back volatile acids and the more volatile fraction caught separately; the test for alcohol is made by adding some iodine and then aqueous KOH solution till the yellow color first formed has disappeared, and then heating gently. A faint odor of iodoform will become apparent.

If there is any doubt regarding the presence of naphtha, the oil can be distilled after adding sulphuric acid, by heating directly or running in steam, the amount of naphtha being determined by collecting in a flask with narrow graduated neck (page 267).

If both naphtha and alcohol are present, the oil is distilled with $KHSO_4$ and pumice, the distillate treated with sodium hydroxide which extracts the alcohol from the naphtha, and the naphtha layer then measured; the alcoholic layer is then redistilled, and the specific gravity of the alcoholic distillate determined. Methyl alcohol may be present.*

* Z. Nahr. u. Genussm., **27**, 469 (1914).

(2). **Free Organic Acid.** (α). In the absence of ammonia (which would be easily determined from the odor on heating) the free acid is determined by titration with N/10 alcoholic sodium hydroxide.

(β). In the presence of ammonium soaps, the sodium hydroxide will not only neutralize the free acid but also decompose the ammonium soaps; the change in color with phenolphthalein will not take place until all the ammonium soap has been decomposed. To determine the amount of acid united with ammonium, 20 to 30 grams of oil are heated with concentrated sodium hydroxide solution in a large Erlenmeyer flask with a splash bulb and the escaping ammonia caught in N/10 sulphuric acid, the excess of this being later titrated with N/10 NaOH.

If no bases other than ammonium are present, an aqueous solution of the oil can be titrated in the presence of methyl orange with N/2 HCl. The amount of acid equivalent to the ammonia found subtracted from the amount necessary in direct titration of the oil gives the amount of acid equivalent to the free organic acid.

(3). **The Amount of Ammonia and of Ammonium Soaps** can be calculated from the above data

(4). **Unsaponified Neutral Bodies** are extracted by the method of Spitz and Hönig (page 197) from the oil by shaking with naphtha and N/10 alcoholic (80 volume per cent) sodium hydroxide. The neutral oil remaining in the naphtha solution is tested as usual (pages 196 to 198) for the kind and amount of mineral oil, fatty oil, rosin oil, pine oil, etc.

(5). **Content of Alkali Soaps.*** Ten grams of oil in 100 c.c. of petroleum ether are shaken with 50 per cent alcohol; the soaps pass into the alcohol. The alcohol is evaporated, the residue (of soap) is dried and weighed. If ammonium soap was present, it will have been hydrolyzed, the free acids remaining; to the weight (of soap) formed should therefore be added the amount of ammonia found in (*b*) 2, above. Sodium or potassium may be detected in the hydrochloric acid solution of the weighed soaps.

(6) The various organic acids present are characterized as follows:

Rosin acids are recognized by their external appearance and by the Morawski reaction (page 186); quantitatively by page 471. Fatty sulphonic acids have a high sulphur content; they separate as a heavy oil on adding mineral acid to their solutions, and on heating with HCl split off sulphuric acid. If the iodine value is not much less than 70 and the acetyl value is over 125, it may be concluded that pure castor oil was used in the preparation of the fatty sulphonic acids.

The method of Davidsohn for the separation of naphthenic and fatty acids was described on page 71. The Charitschkoff test† leads to wrong results in the presence of linolic acid. Marcusson recommends that 5 grams of the alkali soaps of the acids in 100 c.c. of water be treated with a 10 per cent copper sulphate solution. The precipitate of copper soaps is filtered, washed with water, dried at low temperature, and shaken with naphtha. The copper salts of naphthenic acids dissolve, salts of fatty acids do not (the linolate colors the solution green). Commercial oleic acid has an iodine value of 75 to 85, naphthenic acid 30 at the most; the specific gravity of liquid fatty acids is 0.90 to 0.92, of naphthenic acids 0.96 to 1.00. The formolite reaction may also be used (see page 110).

(7). **Substitutes.‡** Sulphite-pitch solutions may be tested for calcium and sulphur dioxide by the usual qualitative procedures. HCl precipitates lignin-sul-

* Marcusson, Z. angewandte. Chem. **30**, 288, 291 (1917).

† Seifensiederztg., **34**, 509 (1907).

‡ Löffl, Seifensiederztg., **44**, 7 (1917).

phonic acid, insoluble in ether, naphtha or benzol (opposite to fatty and rosin acids).

The "black liquor" soaps on treatment with HCl precipitate black, humin acids, also insoluble in ether and naphtha. H_2S is usually evolved on treatment with mineral acid.

The alkali soaps prepared from plant mucilaginous materials (linseed oil) are insoluble in alcohol. They do not give the biuret reaction (violet to pink color with alkali and very dilute copper sulphate solution).

Glue is precipitated quantitatively by tannin but other substances act similarly. It gives the biuret test.

O. Paraffin from Petroleum

1. Definition

Paraffin is the name given to the solid hydrocarbon mixtures obtained from mineral oils or tars or from the lubricating oil distillates; these have melting points ranging from 28 to 72° or higher (excluding earth wax, montan wax). Paraffin may mean a refined, colorless, more or less transparent almost oil-free wax. Semi-refined products are also met with but such products contain more or less paraffin oil. Three classes of paraffin may be distinguished: match paraffin of melting point less than 36°; soft paraffin of melting point under 50°; and hard paraffin of melting point over 50°.

The amount of paraffin in different crude oils varies considerably, the per cent contained in different samples examined found being as follows: Java, 40; Rangoon, 10; Boryslaw, 9; Pennsylvania, 4; Canada, 3; Rumania, 3; Baku, 0.3.

2. General

Paraffin is not directly separated from crude oil as the asphaltic and pitch components prevent crystallization; the paraffin is probably present in colloidal solution which on cooling sets to a smeary mass, inclosing mother-liquor, from which the paraffin can only be obtained through pains-taking effort. Although it has been assumed that paraffin exists in crystalline condition in crude oil the more general impression is that a non-crystalline proto-paraffin is changed to a crystalline pyroparaffin on distillation; the latter can be well separated from the heavy distillates, especially if a relatively low temperature and only a small amount of steam is used in the distillation.

The heavy paraffin-containing distillates are given a preliminary purification to remove water, dirt, resins and asphalt.

The crystallization of the paraffin is brought about by artificial cooling (ammonia refrigeration with calcium chloride brine solutions); this

method allows continuous operation. The precipitated crystal mass (slack-wax) obtained by means of filter (or hydraulic) presses is then changed into paraffin oil and paraffin by the sweating process.

Before introducing into the filter presses, the oil may be diluted with (formerly naphtha) crack or gas-oil distillates (to an Engler viscosity of 1.5 to 2 at 50°). Low pressures (4 to 5 atmospheres) then high pressures (10 to 15 atmospheres) are applied. The material if obtained at relatively high temperature has a solidification point of over 50°, has a dry feel and contains over 70 per cent of paraffin, has a yellow to grey color, has a leaflike crystalline form and breaks with a conchoidal fracture. Cooling to below 0° gives more or less well crystallized soft paraffins, which often still have a vaseline-like appearance and which tenaciously retain oil.

To get paraffin wax, the crude (slack) wax undergoes what is called a sweating process. The sweating is done in lead pans which contain a horizontal sieve. The paraffin is melted on water, the water is run off till the paraffin just rests on the sieve, on which it is allowed to solidify; then all water is run out. The pans (in a sweating chamber) are heated by steam, the oil oozes out and a separation thus is accomplished. The method has the disadvantage of wasting paraffin as this is somewhat soluble in paraffin oil.

Another method* for separating the oil has been suggested; in this the solid paraffin in the pans is covered with water of proper temperature. The oil which oozes out, collects on the surface of the water and is carried away by overflow arrangements. By rise of temperatures a further sweating may be brought about. The process may be repeated to make the separation more complete.

In another method the molten filter-press cakes are pulverized by contact with cold water; in this way a separation of the oil is said to be accomplished. The method† has not been found satisfactory industrially.

The paraffin already somewhat purified by the sweating processes is further treated with acid and alkali, with fuller's earth and similar adsorptive reagents, and after bleaching is ready for the market. By fractional sweating and cooling, as well as distillation in a high vacuum, it is possible to obtain paraffin (hard wax) of melting point as high as 73°; in this way are obtained the materials resembling ceresines (obtained from ozokerite), products of high commerical value.

* Porges and Singer, Braunkohle, **1910**, 748.

† Nitsch and Winterstein, Petroleum, **9**, 1637 (1913). Kissling, Chem. Umschau, **24**, 116 (1917). See also Chem. Ztg., **37**, 54, 87 (1913).

The paraffin obtained by sweating is used in the manufacture of candles, to paraffin matches, as an insulating material in the electrical industry, to prepare bottles for hydrofluoric acid, and for similar purposes. The paraffin used for candles is only slightly soluble in alcohol and melts at about 50°. Softer paraffin waxes melting near 30° are more soluble in alcohol; they are obtained by cold pressing of lighter oils and are used for impregnation and for chewing gum, and if not of too low melting point, are added to hard paraffin waxes for candle stock.

3. Tests

(a) *Appearance*

1. **Color.** Pure paraffin wax is colorless, though some specimens may have a faint yellow color; crude and semi-refined products may appear yellow or brown. Graefe thinks that paraffin scales should have a pale yellow color, and soft paraffin a silver grey appearance. Greenish yellow or brown color is due to faulty distillation but may be due to oxidation of unsaturated oils. Singer suggests that cakes of wax of definite size and thickness be cast and compared with color standards in the form of colored solutions in colorless glass bottles.

2. **Odor.** A peculiar odor of the paraffin wax may not be due to insufficient purification; the wax itself adsorbs odorous materials easily. The odor of sweated paraffin is less noticeable than that pressed with naphtha.

For an approximate determination of such materials, Graefe heats 1 kilogram of paraffin to 150°, sends a current of steam through the material for several hours, and condenses the volatile matter with a regular condenser.

3. **Structure and Appearance.** The structure of the paraffin is examined by means of a microscope; the material may be described as crystalline, amorphous, homogeneous, heterogeneous, waxy, or ceresine-like.

Commercial paraffin should not be fatty, should have a slippery feel and appear dry; laid on paper, it should not give a greasy spot at room temperature.

Hard paraffin gives a metallic ring, soft paraffin gives a dampened tone.

(b) *Flash Point*

The flash point of paraffin generally is not determined. Singer gives the following values for Austrian paraffins.

TABLE 57
FLASH POINT OF PARAFFIN

Melting point	Flash point		Burning point
	Pensky-Martens	Open Tester	
43 to 45	181	190	217
49 to 50	185	200	229
50 to 52	188	203	235
52 to 54	192	206	249
54 to 56	185	210	248
56 to 58	191	213	251
58 to 60	191	224	265
60 to 62	.	226	267

These values give some idea of the volatility of the different samples.

(c) Specific Heat Capacity

This may be necessary in calculating the size of refrigeration units. Table 58 shows the magnitude of the specific heat capacity of various paraffins.

TABLE 58

Material	Temperature	Specific heat capacity
Paraffin, solid	−20° to −3°	0 377
" "	−19° to −20°	0 525
" "	25° to 30°	0 589
" "	35° to 40°	0 622
" , liquid	52 4° to 55°	0 700

(d) Melting Point and Solidification Point

The determination of the melting point and the solidification point offers one of the best ways of estimating the worth of a paraffin for candle manufacture and for match manufacture.

1. The determination in a capillary tube has already been described on page 36. The use of too narrow capillaries, and too rapid heating must be avoided since otherwise the values determined will be too high. The difference between beginning and end of the melting must not exceed 4°. Usually melting begins over 50° but poor grades of paraffin may begin to melt at 47°. An electrical method of melting point determination has been described by Singer.*

In the determination of the solidification point of paraffin, it must be remembered that in crystallization, a fractionation takes place; the

* Chem. Umschau., 2, Nr 15, (1895).

middle of the slab has the highest melting point, the edges melting at a lower temperature. Breth* has shown that differences of 0.7 degree may exist. For results which cannot be criticized, it is necessary to melt up an entire slab of paraffin and then take from the well-mixed, melted mass an average sample.

2. The results obtained by the method of Shukoff (page 37) for the solidification point are sharper than those obtained by the capillary method. The methods designed for fats by Dalican, by Wolfbauer and by Finkener (page 383) can also be used here.

(α) **The Halle Method.** Used in Germany for commercial examination of paraffin materials; it is impracticable and difficult. The temperature is determined at which a film of solid forms over a melted drop of paraffin floating on water.

A beaker† contains water warmed to 70°; a piece of paraffin is melted on the surface so that a drop less than 6 mm. in diameter forms. A thermometer is inserted in the water. The solidification point is the temperature at which a film forms over the surface of the paraffin.

(β) **Determination of the Solidification Point by Means of a Rotating Thermometer (Galician Method).** The round bulb of a thermometer is dipped into the melted material heated to from 60 to 70°; after pulling out with some of the paraffin, it is cooled with constant rotation in an inclined Erlenmeyer flask to prevent air drafts. The temperature at which the drop solidifies and begins to rotate with the thermometer is taken as the solidifying point. This is the so-called Galician method.

TABLE 59

SOLIDIFICATION POINTS OF PARAFFIN BY DIFFERENT METHODS

Calculated from the components	Method of			
	Shukoff	Halle	Rotating thermometer	Capillary tube
45	45	45.5	45 3	45 2
46	46	46 6	46 2	46.4
47	47 1	47 8	47 4	47 4
48	48 1	48 9	48 3	48 7
49	49.2	50 8	49 4	49 6
50	50 3	51 6	50 5	50.6
51	51 2	52 9	51 5	51 8
52	52 1	54 3	52 4	52 7
53	53 1	55 2	53.4	53 8
54	54 2	56 2	54 5	54 7
55	55	57.8	55 4	55.6

The Dalican procedure gives lower values than that of Finkener and the latter lower one than that of Wolfbauer. The Halle method is the

* Petrol., **7**, 106 (1911).

† As recommended by the Verein für Mineralölindustrie in Halle a.d.S. also Petroleum, **2**, 14 (1906).

poorest; most accurate is the method of Shukoff, the rotating thermometer giving values from 0.2 to 0.4 degrees higher than the latter. The graphic method (page 37) is also good, Table 59 by Graefe gives a comparison of the results with different methods.

Graefe has shown that with mixtures of montan wax or of hard paraffin with less valuable soft paraffin, the material can be properly characterized only by means of a method such as the Shukoff, which includes an observation of the heat of solidification.

Recently anilides of the higher fatty acids have been used to raise the melting point of candle material; these also raise the apparent solidification point because they appear to crystallize at temperatures at which the paraffin is still entirely melted.

3. **The Dripping Point** is best determined by the method of Ubbelohde (page 37).

(*e*) *Contraction*

The contraction of melted paraffin on solidification may be* 11 to 15 per cent; high melting waxes may show an even greater contraction.

(*f*) *Heat of Fusion*

This has been determined† by the method of page 49.

The paraffins examined were treated with sulphuric acid and recrystallized from naphtha to obtain an oil-free product. The molecular weight of the paraffin was determined by the freezing point method by solution in naphthalene; then by dissolving naphthalene in paraffin the molecular freezing point constant of paraffin was determined. From this the heat of fusion was calculated by the formula given on page 49. The values obtained are given in Table 60.

TABLE 60

Solidification point of paraffin °C.	Specific gravity at 70°	Molecular weight	Molecular freezing point constant	Heat of fusion calories
52 24	0 7735	325 6	54.35	38.92
55.21	0 7736	329.4	54 15	39.78
57 30	0 7742	388.9	53 68	40.65
59.60	0 7745	421 2	53 77	41.15
60 92	0.7745	428 6	53 41	41.75
62 20	0.7747	445 5	52.97	42.42
65.36	0.7750	500 9	52.18	43.88

* Graefe, Chem. Umschau., **17**, 3 (1910).

† Kozicki and Pilot, Chem. Umschau, **24**, 71 (1917).

(g) *Effect of Light and Heat*

Many kinds of paraffin change when exposed to light; the changes are not all due to oxidation, since a yellowing may take place in a vacuum. The oil-content, degree of purity, foreign admixtures all may be concerned. Singer found that heavy paraffins change color more quickly than the lighter ones. Graefe tests paraffins by pouring into slabs or sticks, covering one-half with opaque paper, and exposing to sunlight for several weeks (longer in winter). Comparisons are thus possible. Poorly refined products change most; probably all materials change to some extent.

Sommer* claims that the yellowing of opaque paraffin is due to unsaturated cyclic hydrocarbons contained in the material; their amount may be determined by the formalite method.

To 20 grams of melted paraffin in a flask are added 20 c.c. of concentrated sulphuric acid; the same amount of formalin is then added, shaking vigorously to avoid too great a rise in temperature. A dark red color develops. After 20 minutes on a water bath, the flask is emptied into a porcelain dish which is heated to separate the reaction products. The paraffin cake is removed when the mixture is cold, the liquid is transferred to a separatory funnel in which after dilution with water, it is shaken with chloroform. After evaporation of the chloroform from the extract, the formalite is dried at 105°, and weighed.

Olefin hydrocarbons are removed by refining with sulphuric acid so do not react here with the formaldehyde. Transparent paraffins showed formalite values of at most 0.3, opaque paraffins gave values up to 1.6.

Behavior on heating: see the bending test page 307.

(h) *Impurities*

These must be expected in the slack wax. A weighed sample of material is dissolved in a large volume of benzol (or carbon tetrachloride) and then filtered hot. The paper is repeatedly washed with the solvent (till a drop of liquid leaves no greasy spot on paper on evaporation); it is then dryed at 105° and weighed.

(i) *Amount of Wax in Crude Paraffin*

The value of a paraffin wax is proportional to the content of the solid wax or pure paraffin contained. The amount of hard paraffin in a 30 to 50 gram sample of the crude paraffin may be estimated by pressing between sheets of filter paper or in linen cloth at a temperature of 2° to 3° to remove the oil; the amount of paraffin scale is determined by reweighing.

* Petroleum, 7, 409 (1911).

(*k*) *Paraffin Content*

1. **Precipitation Method.** The paraffin contained in different products is usually determined by the method of page 108 by dissolving 0.5 to 1 gram of substance in ether, precipitation with alcohol, repeating the operation in the filtrate of the first precipitation. Schwarz and Huber recommend the butanone method (page 110) as the paraffin may be determined by one precipitation.

With soft paraffin (which may be considered a by-product) the method of alcohol precipitation gives only approximate results, as the soft-paraffins are still decidedly soluble in alcohol-ether at − 20°. The industrial process, however, does *not produce more paraffin than can* be precipitated by the alcohol-ether method. Industrial experience with the butanone method has not been recorded.

The amount of soft paraffin in crude wax or candles (page 306) may be determined by the method of Holde,* after extracting stearic acid by means of alkali, by precipitating the harder paraffins, by means of 94 per cent alcohol, in ether solution at + 20°.

2 grams of paraffin free from stearic acid are dissolved in 20 to 30 c.c. of ether and precipitation of paraffin brought about at + 20° by adding 30 to 40 c.c. of alcohol. The quantities and melting points of the precipitated and dissolved paraffin are then determined.

If the soft paraffin does not contain more than 14 per cent of oil, 0.5 gram of substance is dissolved† in 100 c.c. of absolute alcohol and after adding 25 c.c. of water, the mass is cooled to from − 18° or − 20°. The paraffin is then filtered in the apparatus described on page 109, without using suction, and then is washed with cooled alcohol, till the filtrate remains clear on the addition of water. The paraffin is dried, at 35° to 40° in a vacuum desiccator, to constant weight.

2. In factories where the sweating process is used, a laboratory test similar to the industrial operations is used to determine the value of a slack wax.

A small laboratory-scale metal box, double walled so that water may be introduced, contains a sieve on which is placed about 1 kilogram of the crude paraffin (previously poured into a proper form, and solidified). The temperature of the water (and box) is gradually raised by means of a small flame underneath. The oil dripping out of the wax is caught underneath.

Fraction I, from the beginning of the sweating till the sweated oil solidifies at 33°.

Fraction II, from the solidification at 33° till the time the contents of the box appear transparent.

This division is due to the practical discovery that the paraffin which is in the fraction up to time of solidification at 33° cannot be recovered by repeated sweat-

* Mitteilungen, **20,** 5, 241 (1902).

† Z. angewandte Chem., **10,** 300, 332 (1907); **11,** 549 (1898).

ing. This limit is however somewhat dependent on the crude wax, as it may in some cases be set at 40°.

The " Fraction II " from the first sweating is remelted, is allowed to solidify and is then resweated. There is again obtained a

Fraction I up to solidification point 33°

Fraction II up to transparency of the contents of the box.

In the box remains a transparent paraffin which is added to the product of the first fractionation. Fraction II is again sweated. This process is repeated from 3 to 5 times, so long as sufficient material is present in Fraction II for resweating. When no more Fraction II is available, the paraffin content of the combined first fractions is determined by the alcohol-ether precipitation method; also the paraffin of the last Fraction II. Of the amounts thus determined from 60 to 65 per cent can be recovered industrially.

The combined yield of paraffin is calculated by adding together as follows:

1. The combined weights of transparent paraffin left in the box after the various sweatings;
2. 60 to 65 per cent of the paraffin content of the combined first fractions;
3. 60 to 65 per cent of the paraffin content of the last fraction II.

The amount of paraffin oil is obtained by difference.

(l) *Amount of Oil*

Transparent paraffin is preferred as it is supposed that it contains less oil than the opaque material. The milkiness of paraffin is caused by the oil. Redwood* determines the oil by pressing paraffin. The values thus determined differ from those obtained by the alcohol-ether precipitation method. " Oil-free " paraffin was actually found to have as high as 3.6 per cent of oil by the more accurate methods.

" Oil-free " is therefore a matter of definition. A paraffin containing from 2 to 3.5 per cent of oil may be considered industrially as free from oil.

Graefe melts from 200 to 300 grams of the sample and then cools it to − 5° to − 10° for 4 hours. The cake is cut out of the form, wrapped in filter paper and linen filter cloth, and pressed in a cooled press for 5 minutes. The press cake is weighed. From the difference in weight may be calculated the amount of oil.

(m) *Sulphur*

Some samples of paraffin from Java crude oil before the war were found to tarnish silver candle-sticks as the paraffin dripped from the candles. A simple test consists of allowing some of the paraffin at

* Petroleum, **4**, 1038 (1909); Chem. Umschau., **16**, 202 (1909).

170° to act on a silver coin or bright copper foil. If these tarnish, sulphur is probably present.

For a quantitative determination, see page 77.

(n) *Other Tests*

Tests for "stearine," ceresine, rosin, differentiation of petroleum and lignite paraffin, tests for candle stock, see page 303 and following.

P. Vaseline and Vaseline Oil

I. General

Vaseline * is a salve-like product of petroleum manufacture, being colorless or a light brownish yellow; it is used as a basis for ointments, as a lubricant and for protecting iron and steel from rusting. A distinction is made between natural and artificial vaseline. The former was formerly obtained almost exclusively from American petroleum, by distilling off the lighter oils up to a salve-like consistence of the residue; the vaseline was then bleached by means of bone black, sulphuric acid or fuller's earth.† It is, however, possible to obtain natural vaseline from Galician, Alsatian, and even Russian petroleum.

Vaseline may also be obtained by cooling a naphtha solution of a petroleum residue to below 0°, and bleaching the insoluble vaseline-like portion precipitated. It may also be obtained by driving out with steam the burning oils from the precipitate obtained on cooling crude oil; this impure material is itself chilled and bleached to get the vaseline.

The different natural vaselines are distinguished by different melting points and specific gravities.

Artificial vaseline is also used in pharmacy, and is according to the German Pharmacopoeia a mixture of bleached heavy mineral oil (paraffinum liquidum) with ceresine (paraffinum solidum).

II. Properties

The specific gravity ranges from 0.825 to 0.885. Chesborough vaseline had at 100° a specific gravity of 0.845, a German sample gave the value 0.827. The dripping point, determined according to page 37, lies between 30° and 50°.

* Engler and Bohm, Ding. Poly. Jour., 262, 468 (1886). Also Böhm, Dissertation, Karlsruhe, 1887.

† See Jour. Ind. and Eng. Chem., 6, 35 (1914) for methods now used in the United States.

The analysis includes testing for acidity and the absence of foreign materials and is made according to the methods already described under mineral oils. The specific gravity is generally determined at 100° with a Westphal balance (thermometer in sinker reading to 100°) or with a Sprengel pycknometer (see page 4); the Gintl pycknometer is used for determinations at ordinary temperatures. The use of these must be assumed as understood.

The following is the method of testing vaseline as given by the new German Pharmacopoeia: —

White Vaseline. White, odorless, almost green by transmitted light, neither granular nor crystalline under the microscope, and melting to a clear, colorless liquid with a blue fluorescence. Insoluble in water, little in alcohol, easily in chloroform and in ether. Melting point 35 to 40°. Twenty parts of hot water shaken with 5 parts of vaseline must remain colorless with two drops of phenolphthalein but on adding 0.1 c.c. of N/10 KOH, a red color must develop (test for free alkali and acid). A mixture of 3 c.c. of NaOH and 20 c.c. of water heated to boiling with 5 drops of white vaseline, with shaking, should give no precipitate after cooling and saturation with HCl (saponifiable fats and resins). Rubbed up with an equal volume of concentrated sulphuric acid in a dish previously cleaned with sulphuric acid, white vaseline will at most get brown, but will not blacken (organic impurities).

Yellow Vaseline. A yellow transparent mass of salve-like consistence. On heating it melts to a clear yellow odorless liquid with a bluish fluorescence. Under the microscope it should appear neither granular nor crystalline. Solubility, melting point and tests for impurities are the same as for white vaseline.

III. Differentiation of Natural and Artificial Vaseline

According to Engler and Böhm natural and artificial vaselines can be distinguished by the following properties: —

1. The solid parts of artificial vaseline (ceresine) are the cause of a somewhat granular appearance and can be more easily separated by distillation from the liquid particles than those of the natural vaseline.

2. On heating artificial vaseline, it passes suddenly into the liquid condition and before melting has a decidedly firmer consistence than has natural vaseline; but after melting, it is less viscous than natural vaseline which, on melting, acts more like an animal fat. A comparison of viscosities gave the following values: —

TABLE 61

	Viscosity (degrees Engler)			
	45°	50°	80°	100°
Natural American vaseline	4.8	3.7	2.1	1.6
Artificial vaseline	did not flow		1.5	1.2

Thus the artificial vaseline did not flow out of the Engler apparatus at 65°, but at 80° it was entirely melted and less viscous than the natural vaseline.

3. The ability to absorb oxygen was greater with natural than with artificial vaseline. R. Fresenius* after heating 4 grams of Chesborough vaseline for 15 hours, and similarly a German vaseline (Virginia), to 110° in oxygen found 21.8 c.c. of oxygen absorbed and a decidedly acid reaction in the first case, and only 3.2 c.c. absorbed and a faint acid reaction in the latter.

Engler and Böhm heated 11 to 15 grams of acid-free natural and artificial vaseline and other comparison materials with the addition of 2 to 3 grams of water (to increase the oxidation and the tendency to acidity) together with 53 to 76 c.c. of oxygen, in sealed tubes for 24 hours at 110 to 115° and the following results were obtained: —

TABLE 62
OXYGEN ABSORPTION OF VASELINE AND OF LARD

Material	Oxygen absorption per 100 grams, in c.c.	Milligrams of KOH neutralized by 100 grams after O_2 absorption
Natural vaseline	35 to 46 5	5 5 to 10 5
Artificial vaseline	4 2 to 4.7	0 7 to 1 4
Lard	42 to 50	31 to 39

The tendency of natural vaseline to become acid is decidedly less at lower temperatures.

The natural vaseline is therefore under normal conditions sufficiently resistant to atmospheric changes to allow its use in medicine and it also shows greater physical and chemical homogeneity and viscosity at higher temperatures; the greater resistance of the artificial vaseline towards sulphuric acid, nitric acid, etc., is of no importance in this connection. In using vaseline as a lubricant, the natural product is to be preferred because of its higher viscosity, provided that the temperature is not so high as to cause the formation of acidic materials.

IV. Definition of Certain Petroleum Products

The following definitions are used in the German custom houses for classifying certain materials obtained from petroleum: —

• Vaseline oil and paraffin oil are petroleum distillates which have a boiling point above 300°; they are obtained as a liquid oil by pressing out the paraffin wax from

* Ding. Poly. Jour., 236, 503 (1880).

distillates rich in paraffin, or as a salve-like mixture on distilling oils rich in paraffin. Only oil boiling over 300° should be classified as vaseline oil. Paraffin oil is also obtained from lignite tar. Paraffin oil and vaseline oil may be obtained as semi-solid intermediate products or as oily end-products of water-white, yellow, red-yellow or dark brown color, depending on how completely they have been freed of paraffin and on the chemical refining to which they have been subjected. Vaseline oil is quite mobile; the Engler viscosity at 20° C. ranges from 2 to 5 depending on the source. Definite values for viscosity, flash point and density can not be given because of the variety of properties as well as confusion of names.

Galician vaseline oils had densities ranging from 0.882 to 0.900, E_{20} from 2.5 to 8, flash point from 145 to 190°; Russian vaseline oils, densities from 0.861 to 0.870, solidification point under − 30°, flash point from 120 to 160°, E_{25} about 4.5.

Cylinder oil is a high-boiling residue or a distillate of red-brown to very dark color and salve-like consistence.

Vaseline: — A salve-like product; either a residue from petroleum or a mixture of ceresine and paraffin.

Slack wax is a crude paraffin which is worked up into hard and soft paraffin wax.

Paraffin scales represent a crude hard wax which may be filtered to produce refined wax; most of the oil has been separated.

Soft paraffin has a melting point under 40°.

Special methods are prescribed by the Prussian government for distinguishing between these materials.

Q. Tar and Pitch-like Distillation Residues

Petroleum Tar, Petroleum Asphalt and Petroleum Pitch

I. Definition

Dark residues from the steam distillation of crude petroleum are used in the preparation of asphalt, in dark lubricating oils and wagon greases, in the manufacture of roofing-felt and in insulating material; they are available for lubrication if they possess a tarry consistence, or if they become liquid by warming on a water bath, of if they yield over 50 per cent of lubricating oil on distillation by the cracking method. By solution in less viscous lubricating oils they may be used as railway lubricating oils. Such residues are found on the market under the names of petroleum pitch or petroleum asphalt.

Attempts to make an asphalt from petroleum, with properties like that of the natural asphalt, by blowing in air or heating with sulphur have not been successful* as the product has too low a ductility and no adhesive (cementitious) powers. Petroleum asphalts of low paraffin-content are used as fluxes for the brittle natural asphalts. Richardson divides petroleum residuals into: paraffin fluxes (from Ohio and Pennsylvania) which are of no value as binders for highway construction;

* Richardson, J. Ind. Chem. Eng., 5, 462 (1913).

semi-asphaltic fluxes, (Texas), of higher specific gravity and lower content of paraffins, do not satisfactorily dissolve and flux such solid bitumens as gilsonite and grahamite; and asphaltic fluxes (California) which show the highest specific gravity, contain unsaturated hydrocarbons but no paraffin scale, and yield a high coke residue because of high asphalt-content.

In order to obtain a uniform terminology for pitch-like and asphalt-like bodies, it is advisable to restrict the term asphalt to those products which are found already formed in nature and which contain at the most only traces of added mineral oils (these latter being added only to increase their usefulness industrially). The less valuable substitutes which are formed during the treatment of petroleum should be known as artificial asphalt or still better as pitches (for example, according to their origin, as petroleum pitch, fat-pitch, lignite pitch, coal-tar pitch).

Holde and Marcusson have made the following suggestions for fixing the meaning of the term bitumen. In the widest sense it includes the various commercial bitumens given in the attached table, these being either found in nature or formed artificially by destructive distillation or gasification of coal or other materials. In a narrow sense it may be considered the same as natural asphalt and in a somewhat wider sense it may include the artificial products often substituted for asphalt.*

The recognition of the various products by means of the tests given in the table, is perhaps, in some cases made difficult, because the natural products vary in their composition, and all intermediate stages occur. Natural asphalts which give the anthraquinone test are said to occur, while some coal tars contain no anthracene (as is the case if made at too low a temperature). The presence or absence of one of the distinguishing marks should point to the possible origin and not necessarily determine the quality of the product.

II. Specific Gravity

By means of the specific gravity it can be determined whether the residue was obtained by extreme distillation of all volatile components. The specific gravity also serves as a means of identification and is deter-

* In this sense one may speak of the bitumen content of roofing-felt, of insulating material, asphalt powder, etc., this meaning the content of natural asphalt or substitutes for it, such as petroleum pitch, coal-tar pitch, fat-pitch, etc.; those components of coal-tar pitch, oil-gas tar pitch, etc., which are insoluble in carbon disulphide or in benzol and which are rich in carbon, are not considered as bitumens.

mined by the methods described on pages 3 and 5; for small amounts of material the alcohol flotation method is used. If it is only necessary to determine whether the specific gravity is over or under 1.0, one drop of the substance, melted but not overheated, is allowed to fall into a beaker of water at 15°; after one hour the drop will be located either at the top or at the bottom. Air bubbles must be removed with a feather.

III. Melting Point

The higher the melting point, the less suitable will be the pitch as a lubricant for rolling mills or for the preparation of varnishes or of asphalt for building purposes. On the other hand, high-melting asphalts are required for the paving of streets in warm countries. It is not necessary to emphasize how different the requirements are for the different uses.*

The following method for the determination of the melting point† is easily performed and gives concordant results. See Figs. 111 and 112.

Some 6 to 7 mm. wide test tubes are pushed up to a height of 5 mm. into about 25 grams of pitch heated to 150° in an oil bath. (Fig. 112.) After cooling the layer of pitch, a 5 gram layer of mercury is placed on top and the tubes are then heated

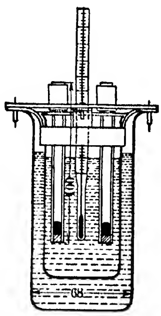


Fig. 111.

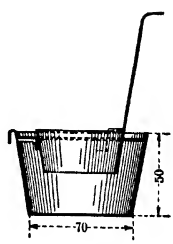


Fig. 112

slowly in the double-walled water bath (Fig. 111) until the mercury begins to drop through the melted pitch. This is called the melting point. Böhm suggests the use of a weighed brass rod instead of the mercury. To avoid the difficulty of filling in the proper height of pitch Barta‡ suggests the use of a 6 mm. wide tube which is 5 mm. high, this being placed on a moistened glass plate and filled with melted pitch at 150°; the heaped-up excess is cut off with a warmed knife. This filled tube is butted against the end of a glass tube (6 mm. wide and 10 cm. long) using a

* Hippol. Köhler, Asphalte.

† Kraemer and Sarnow, Chem. Ind., **1903**, 55.

‡ Petrol., **7**, 158 (1911).

piece of rubber tubing to connect them. The mercury is then put in and the tubes are heated in a water bath, the temperature rising 2° per minute. A glycerine bath is used for pitches melting over 100°.

Of a large number of pitches examined those which could be stirred with a glass rod had a melting point of between 25° and 40°, the solid ones had values from 40° to 80°. The Kraemer-Sarnow method gives sharply defined values, but naturally the values obtained are different from those obtained by other methods, as for example, the capillary tube method.

The dripping point method of Ubbelohde (page 37), used for greases, vaseline and ceresine, can be applied according to the experiments of Loebell to the determination of the softening or flowing point of pitches and asphalts. The advantages of this method over the one just described is that in the Ubbelohde apparatus the fat is under its own pressure when it melts; while in the Kraemer-Sarnow procedure it is under a pressure almost 35 times as great, so that pitches softening at room temperature do not show any differences, the mercury dropping through as soon as it is introduced into the tubes.

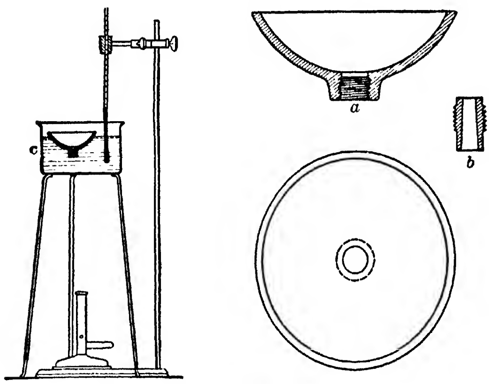


FIG. 113.

The float test* is made on viscous and semisolid refined tars and often on the viscous and semisolid petroleum and asphalt products; when the penetration test can be employed on the two latter classes of material, the float test is not always considered necessary. For the more fluid products the test is made at 32°, and for the semisolid ma-

* Hubbard and Reeve, Methods for the Examination of Bituminous Road Materials, U. S. Dept. of Agriculture, Office of Public Roads, Bulletin No. 38, 1911.

terials, at 50°. When the material under examination is quite hard, the test may be run at 100° C.

The float consists of two parts, an aluminum float or saucer (Fig. 113) and a conical brass collar (*b*). The two parts are made separately so that one float may be used with a number of brass collars. In making the test the brass collar is placed, with the small end down, on the brass plate, which has been previously amalgamated with mercury by first rubbing it with a dilute solution of mercuric chloride or nitrate and then with mercury. A small quantity of the material to be tested is heated in the metal spoon until quite fluid, with care that it suffers no appreciable loss by volatilization and that it is kept free from air bubbles. It is then poured into the collar in a thin stream until slightly more than level with the top. The surplus may be removed, after the material has cooled to room temperature, by means of a spatula blade which has been slightly heated. The collar and plate are then placed in a tin cup containing ice water maintained at 5°, and left in this bath for at least 15 minutes. Meanwhile, another cup is about three-fourths filled with water and placed on the tripod, and the water is heated to the temperature at which the test is to be made. This temperature should be accurately maintained, and should at no time throughout the entire test be allowed to vary more than ½ degree. After the material to be tested has been kept in the ice water for at least 15 minutes, the collar and contents are removed from the plate and screwed into the aluminum float which is then immediately floated in the warmed bath. As the plug of bituminous material becomes warm and fluid, it is gradually forced upward and out of the collar, until water gains entrance to the saucer and causes it to sink. The time in seconds between placing the apparatus on the water and when the water breaks through the bitumen is determined by means of a stop watch and is taken as a measure of the consistency of the material under examination.

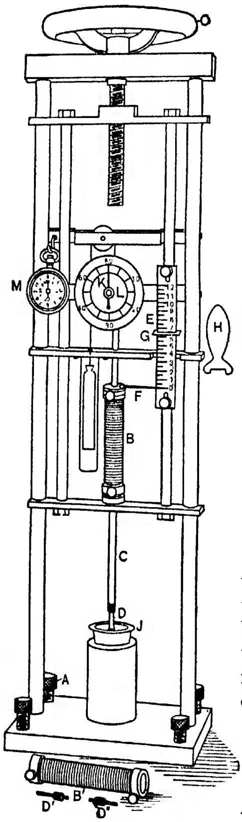


FIG. 114.

IV. MECHANICAL TESTS

Authorities, like C. Richardson, H. Abraham and E. Graefe, place great weight on the mechanical testing of asphalts; among these are to be mentioned the test of hardness and of ductility.

(*a*) *Hardness*

1. The hardness of bituminous materials is measured by the instrument of Abraham (Fig. 114).

In this apparatus is measured the force (exerted by the spring B) necessary to send a steel rod c of fixed head area, in a definite time (1 minute), 1 centimeter deep into the asphaltic mass, kept solid or liquid by immersion in a water bath at constant temperature.

The rods are to be obtained in three sizes of head area. A rod is fastened to the spring B and is forced down by turning O. The tension of the spring (which may be had in two sizes — 1 gram for soft, 1 kilogram for hard, substances) is measured on the subdivisions of E and the time on M. The spring is compressed by the screw O at such a rate that when the rod is immersed 1 centimeter, the pointer K will in 1 minute have reached the mark 60 on the dial L. The divisions are arranged with this end in view.

2. **Penetrometer of Richardson.** This apparatus (Fig. 115) measures the depth to which a weighted needle penetrates.

The substance to be tested is melted in a metal container and allowed to stand for 30 minutes at 25°. The container is placed on the support (C). The needle holder (E) carries a weight (N); the needle is clamped by (M). The registering device (L) is pushed down until it strikes (E).

The needle is brought to a position just touching the bituminous material with the aid of the mirror (D). The position of (L) as it touches (E) is noted on the attached dial (I). By releasing (G) the needle (total weight with holder and added weight equals 100 grams) is allowed to act for 5 minutes. Then (L) is pushed down, again till it touches (E). The reading on the dial is again noted. From the difference in height the degree of penetration is determined; 1 mm. = 1 degree.

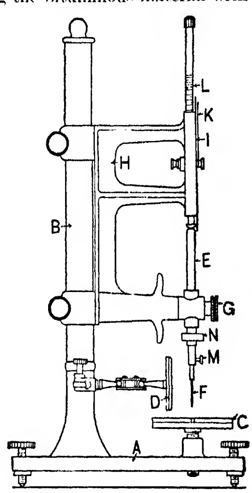


FIG. 115.

3. The object of the penetration test* is to ascertain the consistency of the material under examination by determining the distance a weighted needle will penetrate into it at a given temperature. A standard No. 2 cambric needle is employed for this purpose and this needle is usually weighted with 100 grams. The depth of penetration is determined upon the bitumen maintained at 25°, while the load is applied for 5 seconds.

The Dow penetration machine is shown in Fig. 116. It consists of a No. 2 needle a, inserted in a short brass rod, which is held in the aluminum rod b by a binding screw. The aluminum rod is secured in a framework so weighted and balanced that, when it is supported on the point of the needle the framework and rod will stand in an upright position, allowing the needle to penetrate perpendicularly without the aid of a support.

The frame, aluminum rod and needle weigh 100 grams with the weight c on the

* U. S. Dept. of Agric., Office of Public Roads, Bulletin No. 38, 1911.

bottom of the frame, while without the weight they weigh 50 grams. Fig. 116 shows the needle and weighted frame, together with the side and front views of the entire apparatus, put together and ready for making a penetration. The shelf for the sample is marked *d*; *e* is the clamp to hold the aluminum rod until it is desired to make a test; and *f* is a button, which when pressed, opens the clamp. By turning this button, while the clamp is being held open, it will lock and keep the clamp from closing until unlocked. The device for measuring the distance penetrated by the needle consists of a rack, with a foot *g*. The movement of this rack turns a pinion to which is attached the hand which indicates on the dial *h* the vertical distance covered by the rack. One division of the dial corresponds to a movement of 0.1 mm. by the rack. The rack may be raised or lowered by moving the counterweight *i* up or down. The tin box containing the material to be tested is marked *k*; this is submerged in water contained in the glass cup in order to maintain a constant temperature.

A sample of the material to be tested is warmed sufficiently to flow, and is then poured into the tin box. The box and contents, after cooling, are then immersed in the water maintained at the temperature at which the test is to be made, and allowed to remain immersed for at least 30 minutes. The sample in the tin box should now be placed in the glass cup and removed in it, covered with as much water as convenient without spilling, to the shelf *d*. The brass rod with the needle is inserted into *b* and secured by tightening the binding screw. The rod is lowered until the point of the needle almost touches the surface of the sample; then by grasping the frame with both hands it is cautiously pulled down until the point of the needle just comes in contact with the surface of the sample. This contact can be best seen by having a light so situated that upon looking through the sides of the glass cup, a reflection of the needle will be visible. After thus setting the needle, the counterweight is slowly raised until the foot of the rack rests on the head of the rod and a reading of the dial is taken. The clamp is then opened wide by pressing the button and is held in this position for exactly 5 seconds. The rack is then lowered until it rests on the rod; the difference between the first and second readings of the dial in millimeters is taken as the distance penetrated by the needle. 3 to 5 tests should not vary more than 0.3. It is important that the needle be carefully cleaned before each test. The container for the material consists of a brass cylinder 50 mm. in diameter and 30 mm. high, resting upon a brass plate. The interior of this cylinder is portioned off into 5 compartments of about 12 c.c. capacity each, one consisting of a small brass cylinder 23 mm. in diameter and concentric with the large cylinder. Tests may be made at other temperatures. With harder substances the load on the needle may be 200 grams, with softer only 50 grams.

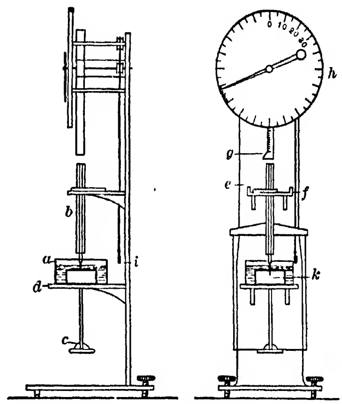


FIG. 116.

(b) *Ductility. Tensile Strength*

This apparatus shown in Figs. 117a and 117b is used in the United States by the Barber Asphalt Company and has, according to C. Richardson and E. Graefe, been found very useful. Petroleum residues containing much paraffin tear apart easily when placed in *B*, while natural asphalts and petroleum residues free from paraffin show a greater tenacity.

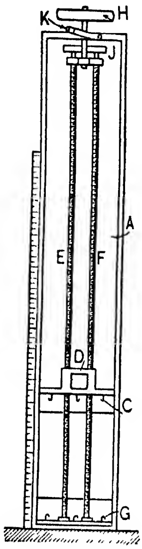


FIG. 117a.

Method of Testing. The basin of the ductilometer is filled with water at 25° and kept at this temperature. The bitumen is poured into the collapsible form *BB* which is hung by rings to the hooks *C* attached to the cradle *C* and the cross-piece *G*, so that on turning the wheel *H*, the cradle is moved and the test briquette pulled apart. The turning of the hand-wheel *H* should be uniform (4 turns in 5 seconds), every turn being indicated by a clap of the hammer *K*. The pulling apart is continued to the breaking point. The distance between the two ends is then measured to obtain the ductility in centimeters. A check result should be obtained. The brass form, after being tied

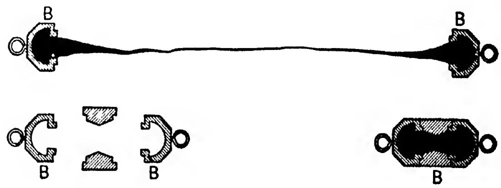


FIG. 117b.

together, is placed on a glass plate and is then filled with pitch. It is advisable to grease the side pieces of the mould which will then fall off in the testing. Deformations of the briquettes are to be avoided.

The ductility of Trinidad and Bermudez asphalt is about 60 centimeters; with carefully prepared petroleum pitches it is 25 centimeters; Grahamite and Texas petroleum residues show only 7 centimeters ductility. Still less ductile are the blown oil-residues which show a value of 3 centimeters.

Gray has shown in a series of experiments (at 15°, 20°, and 25°) on the hardness and ductility of asphalts and petroleum asphalts: —

1. Ductility and softness do not run parallel.
2. Substances with medium softness may have great ductility.
3. Two materials (natural asphalt and petroleum pitch) dissimilar in origin and general properties had the same softness but different ductility; the petroleum pitch requires an addition of 3 times as much

oil as does asphalt to give a compound of the same degree of softness (50) and approximately the same ductility.

4. Another petroleum pitch, in the original condition of the same degree of softness as another natural asphalt, by the addition of oil was made softer and more ductile than the asphalt was made on adding very much more oil. Softness and ductility are influenced quite differently by the addition of oil.

5. The properties of the asphalts and pitches come to the fore only when these materials are mixed with an oil of low viscosity.

V. Chemical Tests

(a) *Mechanical Impurities*

Petroleum pitches contain salts, from the brines associated with oil, and also fine sand.

Two grams of pitch are dissolved in 50 volumes of hot benzol under a reflux condenser and the solution is poured through a weighed filter paper. The residue is washed with hot benzol, till the filtrate is colorless. The residue is dried at 105°, and weighed. Treatment with water will give some information concerning the nature of the residue.

(b) *Paraffin*

In order to determine the amount of paraffin in petroleum residues it is advisable (F. Schwartz), by treatment with conc. sulphuric acid and animal charcoal, to remove the coloring matter and resinous bodies, since these prevent the separation of the paraffin in a pure condition.

Ten grams of pitch and 4 c.c. of concentrated sulphuric acid are heated in a small vessel on an oil bath, with constant stirring, to 180° until the odor of SO_2 can no longer be detected. Forty grams of bone black are then added and the mixture, after pulverizing (and standing over night), is extracted in a Graefe apparatus using naphtha boiling below 50° as the solvent (see page 107). After evaporation of the naphtha, the light-colored residue is analyzed for its paraffin content according to page 108. The amount of paraffin is then recalculated to the original pitch.

(c) *Detection of Foreign Tars, Pitches and Asphalts in Petroleum Pitches*

1. **Detection of the Fat-Pitches.** The black residues obtained in the distillation of candle-stock fatty acids, of wool fat, of palm oil, etc., are used, as are the tar and pitch-like petroleum residues, in the preparation of hot neck grease, of insulating material for cables, for roofing-felt, etc. The softer, less brittle, products of this sort are easily distinguished from the pitches obtained by the distillation of petroleum

(which contain a minimum amount of naphthenic acids or organic acids) by always containing fatty acids and esters; they contain besides these bodies high-boiling hydrocarbons, which always form in the distillation of fatty bodies, and also asphaltic oxygen-containing bodies in increased amount (see page 521 under wool fat olein).

(*a*) The fat can be qualitatively detected by the fatty odor developing on heating the sample on a water bath; also by heating the sample alone, or better with powdered potassium bisulphate, over a free flame, the unpleasant odor of acrolein can be detected. The acrolein can be detected by passing the vapors into an ammoniacal silver salt solution, which will be reduced by the acrolein.

The following methods are used in more exact determinations:

(*b*) **By Distillation.** By dry distillation from retorts, the fat-pitches will give distillates with a decided content of fatty acid; petroleum and

TABLE 63

ACID VALUES OF DIFFERENT PITCHES DISTILLED BY THE CRACKING METHOD

	Fraction I (about $\frac{1}{4}$ of the total distillate)	Fraction II (about $\frac{1}{2}$ of the total distillate)	Fraction III (about $\frac{1}{4}$ of the total distillate)
Hard wool-pitch	5.2	1.1	0.08
Mixture of hard fat-pitches	5.3	0.95	0.6
Hard petroleum-pitch	0.4	0.4	0.3
Lignite-tar pitch .	0.1	0.2	0.4
Lignite-tar pitch, II	0.2	0.6	0.6

lignite pitches, on the other hand, give distillates free from acid (see Table 63). These differences become even more pronounced if the pitch is not distilled with the free flame but with steam superheated to 300° (see Table 64)

TABLE 64

ACID VALUES OF DISTILLATES OBTAINED BY THE DISTILLATION OF FAT-PITCHES WITH STEAM

	Fraction I	Fraction II	Fraction III
Hard pitch mixture	14.6	13.7	13.4
Soft wool-fat pitch	34.8	37.8	7.0

It must be kept in mind in making these tests that the crack distillates of some natural asphalts give considerable amounts of acids,

which can, however, be distinguished from the acids distilled from wool-pitches by their brittleness, and slight solubility in petroleum ether.

Considerable quantities of pure white candle paraffin (14 to 17 per cent) can be separated from the distillates* of fat-pitches by the alcohol-ether method (page 108). The following elementary analyses of certain of such distillates show the composition of the solid paraffins and the liquid portion of the distillate (corresponding in large degree to the unsaturated distillates obtained by crack distillation of petroleum pitch).

TABLE 65

	Per cent C	Per cent H	Per cent CH
Paraffin from the distillate of a hard wool-pitch	85.02	14 3	99.32
Paraffin from the distillate of a mixture of hard fat-pitches	{ 85 37 84.51	14 89 14 93	100.26 99.44
Liquid from a hard wool-pitch freed from fatty acids and paraffin........	85.89	13 07	99.96

The specific gravities of the fractions from fat-pitches, petroleum and lignite pitches distilled with a free flame are considerably less than unity, while the specific gravities of the aromatic distillates from coal-tar pitch are greater than 1. The latter are also easily soluble in alcohol with gentle heating and are sulphonated with concentrated sulphuric acid.

At times, in order to be admitted free of duty (Germany), petroleum residues are increased in specific gravity by adulteration with rosin to values above unity. If, therefore, the specific gravity is over 1, the pitch must be extracted with boiling 70 per cent alcohol, the alcoholic extract evaporated and the Morawski reaction applied to the residue (see page 186). The acid value is also increased by the addition of colophony.

(*c*) **By the Saponification Value.** The hard fat-pitches still contain considerable amounts of fatty acids and esters and, therefore, give higher saponification values than do petroleum residues; this, therefore, gives a means of distinguishing between the two kinds of material.

According to the assumption of G. Kraemer, who obtained ester values† of 2 to 4 with asphalt from Wietze crude oil and attributed

* Donath, Chem. Ztg., **17,** 1788 (1893).

† Chem. Ztg., **31,** 675 (1907).

these to the presence of wax esters, the pitches under examination should contain recognizable amounts of esters. Since, however, the ester values of Kraemer and those of the Materialprüfungsamt were obtained with $N/2$ alcoholic KOH which may exert an oxidizing action on the unsaturated bodies, the low ester values in question do not appear to be a sufficient basis for assuming the presence of esters in asphalt and pitch. These bodies may contain considerable amounts of unsaturated components.

Marcusson * proposes the following method for the determination of the saponification value of pitches:

5 grams of pitch are dissolved in 25 c.c. of benzol free from sulphur and then heated with 25 c.c. of $N/1$ alcoholic KOH for 1 hour under a reflux condenser. After cooling, there are added 200 c.c. of neutralized 96 per cent alcohol, 3 c.c. of a 1 per cent alcoholic phenolphthalein solution and 3 c.c. of a 3 per cent alcoholic solution of alkali blue 6 *b* (Hochster Farbwerke) and the mixture is titrated with $N/2$ hydrochloric acid to a distinct blue color. The color is best determined by observation of the liquid draining down the sides after shaking, or by removing a portion of the solution to a test tube. Fat-pitches give with this procedure saponification values from 33 to 106; petroleum pitch and lignite-tar pitch, values from 8 to 21, natural asphalt from 29 to 37.

If the saponification value is near 100, it will be possible to conclude that pure fat-pitch is present. The presence of fat-pitch can always be determined in this way. If the value is lower, the presence of petroleum pitch, in the presence of fat-pitch, can be determined by the following method of Marcusson, provided 20 per cent of petroleum pitch is present.

(*d*) The test depends on the fact that petroleum pitch (and natural asphalt also) does (fat-pitch does not) form insoluble double compounds with a mercury bromide solution (used first by Malencovic for other asphalt investigations) because of the presence in it of sulphide sulphur.

10 grams of pitch are dissolved in 25 c.c. of benzol with gentle heating, cooled, 30 c.c. of $N/2$ alcoholic KOH are added, the mixture is shaken and quickly diluted with 200 c.c. of 96 per cent alcohol. After standing for a short time, the alcohol solution is decanted, the residue in the flask washed with a little alcohol, warmed on a water bath, sucked free from alcohol and then dried at 105°. The residue is dissolved in ether with gentle heating under a reflux condenser, some granular calcium chloride being added, and after settling and cooling, filtered through a pleated filter into a 3.5 mm. test tube, the undissolved asphaltenes being thus separated. The solution thus obtained is treated with 20 c.c. of mercuric bromide (5 grams in 250 c.c. of anhydrous ether) and allowed to stand over night. The precipitate formed is collected on a filter, washed with ether and dissolved in warm benzol. Mercurous bromide which may have been precipitated remains on the paper undissolved. Considerable amounts of petroleum pitch or natural asphalt give a precipitate which dissolves in benzol with a brown-black color.

* Zeit. f. angew. Chem., **24**, 1297 (1911).

(*e*) **Copper Content of Fat-Pitch.** Probably all fat-pitches contain (if only in small amounts) copper soaps from the copper stills used in their distillation. The petroleum residues, on the other hand, are free from copper, since petroleum is distilled only from wrought iron or cast iron stills.

(*f*) **Distinguishing between Stearine Pitch and Wool Pitch.** By boiling with strong alcoholic potash, Donath and Margosches* found that wool pitch does (stearine pitch does not) give a precipitate difficultly soluble in boiling alcohol and in hot water, which on treatment with hydrochloric acid splits off a dark fatty acid. This acid purified by treatment with alcohol and bone black, and recrystallized, gives a snow-white body melting at 80 to 82.5°.

10 grams of pitch are boiled with 50 c.c. of $N/2$ alcoholic KOH for $\frac{1}{2}$ hour under a reflux condenser. If, on cooling, a layer of crystals forms above the insoluble pitch, wool pitch may be considered present.

(*g*) In the treatment of the benzol solution of the pitch with naphtha and conc. sulphuric acid, according to Marcusson-Eickmann (page 271), stearine pitch gave 3.3 to 11.8 per cent of oily material, wool pitch 15.4 to 40 per cent, while petroleum pitches gave more (40 to 60 per cent).

2. Detection of Wood Tar, Pine Tar and Coal Tar or the Pitches Derived from them in Petroleum Pitch.

(*a*) **Wood tar,** resulting from the dry distillation of wood, is recognized by its characteristic creosote odor and its almost complete solubility in cold absolute alcohol and in glacial acetic acid. Petroleum pitch or fat-pitch which may be present, remain to a large degree undissolved on treatment with alcohol. An aqueous extract of the wood tar has an acid reaction (acetic acid) and gives, with a drop of ferric chloride, a green coloration, which latter assumes a brownish tinge. The first distillates of wood tar form aqueous liquids with an acid reaction. The oily distillates have a more or less strong odor of creosote, are easily soluble in alcohol and on treatment with concentrated sulphuric acid are changed into water-soluble substances.

Wood-tar Pitch differs† from all other pitches in being difficultly soluble in cold carbon tetrachloride. Like pine-tar pitch it has a specific gravity of more than 1 and contains large amounts of rosin acids; the oily parts of the distillates are in part insoluble in naphtha (as are those of wood tar). It gives the diazobenzol reaction (page 201).

(*b*) **Pine Tar,** obtained by the distillation of resinous wood, has a high acid value because of its considerable content of rosin acids (15 to 25 per cent); it begins to boil near 110°. The first distillates up to 200° are in part aqueous and are acid, having an odor of wood tar, as do also the portions boiling up to 300°. The specific

* Chem. Ind., **1904,** 224.

† Donath and Margosches, loc. cit.

gravity of the oily distillates is over 1.0, they do not completely dissolve in "normal benzine," give a red color with sulphuric acid of specific gravity 1.62 (as do the rosin oils) and give the Morawski reaction very sharply, because of the presence in the distillates of rosin oil formed from the rosin acids present in the pine tar.

The distillates boiling over 300° also have a specific gravity of over 1 but dissolve almost completely in an equal volume of "normal benzine," the solubility decreasing on adding more "normal benzine."

Pine Pitch acts like pine tar. It has a high content of rosin acids (an acid value of 57) and begins to boil at 140°. Between 200° and 300° are obtained distillates which are in part aqueous, in part oily; of the latter 90 per cent is soluble in an equal volume of "normal benzine," only 80 per cent is soluble in 4 volumes of "normal benzine." The higher boiling fractions are almost completely soluble in an equal volume of "normal benzine," but less soluble in 4 volumes.

(*c*) **Coal Tar and Coal-tar Pitch,** the first being recognizable by its creosote odor, contain considerable amounts of soot-like particles insoluble in benzol (see page 268); all other pitches, which have not been distilled to the coking point, are soluble in benzol or contain only a trace of material insoluble in benzol. The sulphur content of coal-tar pitch is as a rule only 0.6 to 0.8 per cent.

Because of its content of the higher phenols, coal tar gives the Graefe reaction with diazobenzol chloride, described on page 201.

Alcoholic extracts made of wood-tar and coal-tar pitches contain considerable amounts of substances of specific gravity greater than 1. The distillates from coal tar are easily soluble in alcohol and are changed to water-soluble bodies on heating with concentrated sulphuric acid. The portions boiling over 200° have a specific gravity of more than 1; while the distillates from petroleum pitch, lignite pitch and fat-pitch all have specific gravities of less than 1, are difficultly soluble in alcohol and contain considerable quantities of materials not sulphonated by sulphuric acid.

To determine the amount sulphonated several grams of the pitch are warmed for 1 hour with 5 volumes of concentrated sulphuric acid on a water bath, and poured into 500 c.c. of water (see also page 286 under "quantitative determination of asphalt"). To determine the nature and amount of the unsulphonated bodies, Holde suggests that the entire liquid be poured into a 500 c.c. flask with a long narrow neck graduated to 0.1 c.c. (Fig. 118). On heating the flask with warm water, the unsulphonated particles collect in the neck and can be conveniently run off sideways through the tube by adding water.

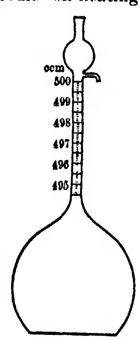


FIG. 118.

Mixed with other pitches, coal tar or coal-tar pitch can be detected by the above characteristics, and certainly by the following anthraquinone test. A part of the distillate passing over 300° or the solidified portion of the same (this can be easily separated from the liquid portion by treatment with a little absolute alcohol) is oxidized* and the anthraquinone obtained detected by the Liebermann reaction, a bright red coloration being formed on boiling with zinc dust and sodium hydroxide.† After filtering, decolorization will gradually take place in the air.

To carry out the oxidation 1 gram of the substance is dissolved in 45 c.c. of

* Luck, Zeit. f. anal. Chem., **16**, 61.

† Annalen, **212**, 65.

glacial acetic acid and to the boiling solution is added in the course of two hours, drop by drop, a solution of 15 grams of chromic acid in 10 c.c. of glacial acetic acid and 10 c.c. of water; the mixture, boiled two hours, is allowed to cool, 400 c.c. of water are added and the precipitated anthraquinone is collected. If the material contains only small amounts of coal-tar pitch, corresponding greater amounts of material and oxidizing agent are used.

According to F. Schwartz foreign tars and pitches in the presence of coal tar are detected by examination of the portion unattacked by conc. sulphuric acid, according to the methods given on page 263.

10 grams of pitch are treated with 4 c.c. of concentrated sulphuric acid, the amount of residue obtained on evaporation of the naphtha extract (obtained according to page 262 and 263) serves as a measure of the amount of foreign pitch present.

According to Schwartz the amount of substances not attacked by concentrated sulphuric acid varies:

with coal-tar pitches from 0.10 to 0.21 per cent,
with natural asphalts from 0.6 to 11 per cent (generally from 3 to 5 per cent),
with petroleum pitches from 5.7 to 36 per cent (generally from 15 to 30 per cent).

If, therefore, values are obtained which are decidedly more than 0.2 per cent, it will be necessary to assume the presence of another bitumen in the coal tar.

If the different kinds of coal tars are to be distinguished (gas tar, blast-furnace tar, etc.) from one another, a determination of the amount of free carbon and of ash is of value. Gas-tar pitch (with the exception of the vertical-retort-tar pitch which is like coke-oven-tar pitch) rarely contains less than 25 to 30 per cent of fixed carbon, coke-oven-tar pitch, as a rule, contains 5 to 7, rarely 10 to 12 per cent. Gas-tar pitch and coke-oven-tar pitch give rarely more than 0.1 (up to 0.5) per cent of ash, blast-furnace-tar pitch, however, gives quite high values (at least 6.8 to 11.1 per cent).

3. **Lignite-tar Pitch.** This can be distinguished from coal-tar pitch by its not containing carbonaceous particles insoluble in benzol. It gives the diazobenzol reaction* (as does coal tar) because of its content of phenol-like bodies.

2 grams of bitumen are boiled 5 minutes with 20 c.c. of $N/1$ aqueous NaOH, and filtered when cool. If the filtrate is very dark colored, shaking with finely powdered NaCl will lighten the color. The filtrate is treated with diazobenzol chloride solution (freshly made from anilin, hydrochloric acid and potassium nitrite); in the presence of phenols a red color appears, and under some conditions a red precipitate forms.

* Graefe, Chem. Ztg., **30**, 298 (1906).

Natural asphalt, petroleum pitch and fat-pitch * give only a yellow or orange but not a red color.

Loebell has improved the method for the detection of lignite-tar pitch and coal-tar pitch in the presence of natural or petroleum asphalt.

The sample is pulverized, if necessary with the addition of sand. Several grams of the pulverized material are extracted with acetone, the extract of lignite-tar pitch being red brown, of natural and petroleum asphalt, colorless or lemon yellow. The residue obtained on evaporating the acetone, after treatment with $N/2$ aqueous alkali, gives with diazobenzol chloride a red color in the presence of lignite-tar pitch or coal-tar pitch; with natural asphalt an almost colorless solution is obtained.

A positive diazo-test does not necessarily mean an adulteration† with lignite-tar pitch, since often lignite-tar oils (paraffin oils) are added to natural asphalt in order to make it more workable.

In order to determine in such a case whether an allowable addition of lignite-tar oil has been made or the material has been adulterated with lignite-tar pitch, the diazo-test is made with the asphaltenes insoluble in petroleum ether (see method of Marcusson and Eickmann, page 271). If the asphaltenes also give the diazo-reaction, lignite-tar pitch is present.

In order to obtain all the phenols from the asphaltene precipitate (formed by the addition of petroleum ether to the benzol solution of the pitch, according to page 271), the mass is boiled for $\frac{1}{4}$ hour under a reflux condenser with alcoholic KOH, filtered after cooling, the alcohol evaporated from the filtrate and the residue dissolved in water. The (generally dark colored) solution thus obtained is shaken with NaCl to lighten the color, most of the impurities being precipitated. The light-colored filtrate is then tested as usual by means of the diazobenzol chloride reaction.

In the testing of asphalt mastic for lignite-tar pitch it must be remembered that the mastic is prepared by the heating of a bituminous limestone with a natural asphalt or with a substitute for asphalt. If lignite-tar pitch is used, the phenolic bodies present may chemically unite with the limestone with the formation of calcium phenolate. If the mastic is then extracted with benzol or chloroform, very few phenols will be found in the extract; consequently, the diazo-reaction may fail even in the presence of lignite-tar pitch. If, however, the mastic is extracted with an organic solvent in the presence of hydrochloric acid (for example, ether-hydrochloric acid), the phenolates will be decomposed and the diazo-reaction will be given with considerable sharpness.

4. **The Detection of Natural Asphalt** in petroleum-pitches need hardly be considered because of the higher value of the former. More

* Marcusson and Eickmann, Chem. Ztg., **32**, 965 (1908).

† Chem. Rev., **18**, 47 (1911).

important is the reverse detection. The determination of each in the presence of the other is often required. Petroleum pitch can be detected in a mixture of bitumens according to page 271; the presence of natural asphalt can also be determined.

(*a*) **Acid Value (Marcusson).** Ten grams of bitumen are dissolved in 25 c.c. of benzol (free from sulphur) under a reflux condenser; the asphaltic material is precipitated by adding 100 c.c. of neutralized 96 per cent alcohol, and the mixture allowed to clarify over night. The benzol-alcohol solution is decanted, the residue washed with 50 c.c. of alcohol, and the united solutions titrated with $\frac{N}{10}$ NaOH in the presence of alkali blue, to a red color.

Natural asphalts show an acid value from 2.8 to 15.4; petroleum residues, from 0.1 to 0.4.

(*b*) Characteristic of natural asphalt is a considerable content of ash, while petroleum residues are almost free from ash.

(*c*) Natural asphalts contain as a rule from 1.7 to 10 per cent of sulphur; many petroleum pitches, obtained from crude oils free from sulphur or containing only minimum amounts of sulphur, contain only very small amounts of sulphur (1.4 per cent at the most). Mexican petroleum residues, however, may contain 2 to 6 per cent of sulphur.* Petroleum pitches from California or Trinidad sulphur-containing crude oils may contain more sulphur than natural asphalt.

Hungarian petroleum pitches of melting point 34° and 55.4°, of specific gravity 1.02 and 1.03, contained for example 86.3 and 87.3 per cent carbon, 10.3 and 9.7 per cent hydrogen and 3.4 and 3.0 per cent oxygen, but no sulphur or nitrogen. If the origin of the petroleum pitch is known it may be possible to determine from the amount of sulphur whether natural asphalt is present. It must be remembered, however, that petroleum pitch, coal-tar pitch, etc., on boiling with sulphur, are changed into products more suited for the preparation of asphalt; in such a case, the sulphur content would give no information. The artificial addition of sulphur should be shown by the evolution of hydrogen sulphide on treating the pitch with steam.

For the determination of sulphur, see page 77 and following. Graefe† detects sulphur qualitatively by heating 1 gram of asphalt for 5 minutes to 200 or 250° in a test tube; a piece of filter-paper moistened with lead acetate solution is held 1 centimeter above the material. A black color indicates natural asphalt; petroleum pitch or glance pitch does not give the test. Wood and lignite pitches give a positive reaction but these materials can be otherwise characterized.

* Lohmann, Chem. Rev., **18**, 107 (1911). In all other properties, Mexican petroleum residues are like other petroleum pitches.

†Zangewandte Chem., **19**, 21 (1916).

(*d*) The method of Marcusson and Eickmann* is available for the analytical differentiation of natural from artificial asphalt; it depends on the examination of portions of the pitches insoluble in petroleum ether.

20 grams of bitumen are dissolved in a small flask with 30 c.c. of benzol under a reflux; the solution is poured with shaking into 400 c.c. of petroleum ether boiling under 80° and the flask rinsed with 40 c.c. of petroleum ether. After standing, the precipitated asphaltic material is collected, washed with petroleum ether and the filtrate treated three times with 30 c.c. of concentrated sulphuric acid in a separatory funnel to completely remove asphaltic bodies. The petroleum ether solution is washed with $N/1$ alcoholic (50 per cent) alkali and then several times with water; the petroleum ether is then evaporated and the residue warmed 5 minutes on a water bath to constant weight. The easy volatility of mineral oils must be considered here and care taken not to superheat

It is generally sufficient to determine the amount and the consistence of the oily portion to discover whether natural asphalt or petroleum residue is present. Before determining the consistence, the oil (see page 180) is to be heated 10 minutes in a 15 mm. wide test tube (on a water bath) and it is then to be kept for 1 hour without disturbance at 20°.

Natural asphalt gives† from 1.4 to 3 per cent of oily components, yellow brown to brown in color, with a paraffin content of at most 1 per cent; on cooling the alcohol-ether solution to − 20° resinous, transparent bodies precipitate. Petroleum pitch gives 26 to 58 per cent of oily parts, green to greenish-black, not liquid at 20°, of a salve-like consistence, and with vaseline-like separations; the paraffin content of these portions is, as a rule, 3.3 to 16.6 per cent, in some cases it may go as low as 2 per cent. Petroleums from Trinidad and Venezuela, rich in asphalt but almost free from paraffin, give residues, which are nearly free from paraffin, so that they act like natural asphalts. Hard asphalt, softened by the addition of paraffin-containing liquid petroleum residues, may act like petroleum pitch in the method of Marcusson and Eickmann.

A determination is made of the amount of paraffin in the distillate of the portions soluble in petroleum ether; the per cent contained is calculated on the basis of the amount of oil used for distillation, not on the amount of the distillate.

If the oily residue is more than 34 per cent (referred to the ash-free bitumen), and if it shows a salve-like consistence at 20° and gives vaseline-like separations, then the presence of petroleum residue is probable. If only one of the conditions is fulfilled (as, for example, with mixtures) then the determination of the paraffin content of the oily parts will

* Chem. Ztg., **32**, 965 (1908).

† The results are referred to ash-free bitumen.

decide the question; if the paraffin content is more than 2 per cent, petroleum pitch must be assumed present. In this way 25 per cent petroleum pitch in natural asphalt can be detected.

Paraffin oil which is added to natural asphalt to make it more pliable does not affect the differentiation of natural and artificial asphalt. (See Marcusson, above, page 271.)

5. **Examination of Asphaltic Cements for Colophony.** Asphaltic cements are used in the preparation of insulating materials used in the building industry and frequently contain mixtures of natural asphalt, coal-tar distillation residues, or only the latter in a sulphurized condition, colophony being added. The addition of sulphur is said to make the product more resistant to the weather; the rosin is added to increase its adhesive properties.

The colophony present is determined quantitatively by the method of Holde and Meister.*

10 to 20 grams of the sample (in the presence of over 4 per cent of rosin, 2.5 to 5 grams will be enough) are extracted with 200 c.c. of ether under a reflux condenser; the undissolved portions separated by filtration are washed three times with ether. The filtrate is shaken (six times is generally sufficient) with 30 c.c. portions of $N/10$ NaOH (aqueous) until the aqueous layer appears colorless. The soap solution thus obtained is twice shaken with 50 c.c. portions of ether, the united ether extracts once with 30 c.c. of $N/1$ alkali. The united alkaline extracts containing the colophony as soap, are treated with dilute sulphuric acid in a separatory funnel in the presence of ether. After exhaustive extraction with ether the ether solution of the colophony (in the form of abietic acid) is washed free from mineral acid by treatment with Glauber's salt solution, and after filtration, evaporated to 100 c.c. The solution is then boiled with 0.5 gram of dry bone black, the red brown color becoming decidedly less. After filtering and washing out the bone black with ether, the solvent is evaporated on a water bath, the residue dried 5 minutes at 105° and weighed after cooling. To the weight found is added a correction of 8 per cent to make up for the portion of the rosin not soluble in the $N/10$ aqueous alkali.

Eleven artificial mixtures of rosin and coal-tar pitch containing from 1.5 to 14 per cent colophony were examined by this method and the amount found varied from that actually present not more than 0.7 per cent.

(*d*) *Examination of Rock Asphalt and of Asphalt Powder*

As substitutes for natural asphalt are sometimes found mixtures of petroleum pitch (and other residues from the distillation of bituminous materials) with limestone, containing clay and magnesium compounds; these materials, which are in part powdered and in part in larger pieces, are to be examined for the amount and kind of bituminous material contained.

* Chem. Ztg., **35**, 793 (1911).

(*a*) **Determination of the Amount of Bitumen.** 2 grams of the asphalt powder* are treated with 15 c.c. of ether-hydrochloric acid (prepared by saturating concentrated hydrochloric acid with ether, cooling with water) in 3 to 4 portions with constant stirring, until the carbonate present has been completely decomposed; the ether lost by evaporation is replaced by adding 5 c.c. After 10 minutes' digestion, 15 c.c. of water are added and the ether is evaporated by warming and by the addition of hot water; the dissolved inorganic materials are then poured through a filter, the flask, stirring rod and paper are washed free from mineral acid and both dried at 110° for ¾ hour. The bitumen in the flask is then dissolved in chloroform, the solution poured through the filter, the filtrate caught in a weighed glass dish, the solvent evaporated on a water bath, and the residue dried at 105° to constant weight. The agreement, on repetition, of results is very good; the bitumens thus obtained do not contain more than a trace of ash.

(*b*) **Nature of the Bitumen.** To test for natural asphalt, the content of sulphur is established. By treatment with benzol, it is determined if the material is completely soluble in this solvent, or if appreciable amounts of carbonaceous bodies are present (coal-tar pitch). To detect the presence of lignite-tar pitch the diazo-benzol chloride test (page 201) is applied. The presence of fat-pitch is determined by means of the saponification value. Natural asphalt and petroleum-pitch are detected through the separation of the oily portions by the method of Marcusson and Eickmann.

(*c*) **Calcium Carbonate, etc.** To determine the inorganic components, the acid solution obtained by the method of Prettner, or the residue from extraction of the bituminous materials with chloroform, can be used. The quantitative determination of gypsum, calcium carbonate and magnesium carbonate, alumina and iron oxide, gangue, etc., is carried out as usual.

R. By-products of the Petroleum Industry

I. By-products of Distillation

(*a*) **Picene Fraction.** After the main products (naphtha, kerosene, gas-oil, lubricating oil, etc.) have been distilled from the petroleum, some very viscous, brown red, easily solidifying masses. pass; these, however, have at the present time no industrial use and are, therefore, burned under the stills. This fraction contains picene and similar unsaturated bodies.

These masses are said† to contain, besides paraffin which can be leached out by means of naphtha, a complicated mixture of hydrocarbons of the general formula C_nH_{2n-2}; their composition is similar

* Prettner, Chem. Ztg., **33**, 917, 926 (1909).

† Zaloziecki and Gans, Chem. Ztg., **24**, 535, 553 (1900).

to that of anthracene, phenanthrene, retene, etc., but they act entirely different on oxidation with chromic acid in acetic acid solution. They yield neither quinones nor carboxylic acids but are completely changed to carbon dioxide and water. They are, therefore, assumed to be non-aromatic in character. It has not yet been determined whether these bodies may be considered as polycyclic derivatives.

(*b*) **Coke.** If the petroleum distillation is carried on until with even the highest heat no more distillate passes (often the distillation is continued only till pitch remains) there remains a residue of coke which because of its low ash content is used as electric light carbon. To determine its conductivity, it is connected in series with an incandescent lamp (or in the circuit of an electric bell connected with an accumulator or several cells). The lighting of the lamp (or ringing of the bell) shows the conductivity.*

(*c*) **Gases.** In the distillation of petroleum on an industrial scale gases form which are generally used as fuel under the stills or after scrubbing are burnt for power in internal combustion motors. They are examined by the regular methods for gas analysis.

II. By-products of Refining

(*a*) **Acid Resins.** In the refining of high-boiling oils with concentrated and with fuming sulphuric acid, especially in removing the asphaltic resins from dark residues, there are obtained black, resinous bodies. Of these so-called acid resins some (for example, those obtained in the preparation of white vaseline oils) dissolve in water as sulpho-acids with a dark color and can be used in the preparation of water-soluble oils. Others (such as are obtained in the refining of wagon oils (residues) in amounts up to 30 per cent) are pitch-like in character and little soluble in water; after boiling out the free acid with water, or by neutralizing it with lime, they are dissolved in less viscous oils, burned under the stills, redistilled over a free flame or used as substitutes for pitch and asphalt.

Such by-products are admitted free of duty in Germany if they have a specific gravity greater than 1; they are tested for specific gravity, water-soluble components, ash, content of neutral pitch-like bodies, etc.

The separation of the free sulpho-acids depends on the solubility of their barium salts. The aqueous extract to be tested is diluted to 200 or 500 c.c. and divided into two aliquot parts. In one the total acid is determined by titration with $N/10$ or $N/2$ alkali in the presence of phenolphthalein; in the other part the sulphuric acid is determined as barium sulphate. The content of sulpho-acids is expressed in equivalents of KOH or SO_3.

* Graefe, Laboratoriumsbuch, 62.

The pitch-like residues obtained in the distillation of petroleum are distinguished from the acid resins (if the excess sulphuric acid in these has been neutralized with lime) by their content of calcium salts of sulpho-acids and of alkyl-sulphuric acids.

F. Schwarz* decomposes these salts into calcium chloride and the free acids by heating them with alcoholic hydrochloric acid (sp. gr. 1.19).

The acids remain in the alcoholic solution and are separated from the oily and resinous bodies by filtering after cooling; the filtrate is neutralized and then separated by the method of Spitz and Honig from the unsaponifiable bodies extracted by the alcohol.

(*b*) **Neutral Pitch-like Bodies.** Bodies that can be directly used as pitch or asphalt for varnishes, etc., are obtained* by refining dark residues with fusel oil (amyl alcohol, see also page 36). In the testing of these bodies, the determination of the melting point (according to page 256 is of chief importance. Other tests, ash, foreign substances, etc., are made according to methods outlined on page 262 and following.

(*c*) **Acid Sludge.** Besides the acid resins considered under (*a*), impure acids (sulphuric acid, sulpho-acids and sulphur dioxide) are also formed during the refining of petroleum. These acids often still contain considerable amounts of acid resins, so that frequently in determining the freight rate for such a material it is a question whether it should be called an acid resin or a by-product acid.

These by-product acids (in so far as they are not buried to get rid of them) are concentrated and mechanically purified for the sulphuric acid in them, or treated with scrap iron or copper for the preparation of sulphates of these elements. The regenerated acid is used again in the refining process. It has been suggested that by treating these spent acids with saw-dust, there might be a recovery of sulphur dioxide, which could be used in various ways.

Example. 1. **External Appearance.** Viscous, black, full of black solid particles, odor of sulphur dioxide.

2. **Pitch-like Bodies Insoluble in Water.** 5 grams of the spent acid were treated with 50 c.c. of water, the separated pitch particles were washed free from mineral acid with hot water, treated with hot benzol and freed from the benzol by evaporation. After drying at 105°, 19.3 per cent of a brownish black asphaltic residue was obtained; there was only 0.1 per cent benzol-insoluble material having the same appearance as the benzol-soluble part and containing a trace of ash.

3. **Free Sulphuric Acid.** The aqueous liquid, freed from the pitch-like bodies, together with the wash waters was diluted to 1000 c.c.; 50 c.c. of this was treated hot with barium chloride in the presence of dilute hydrochloric acid. (Barium salts of sulpho-acids do not precipitate in the presence of hydrochloric acid.) The amount of sulphuric acid in the original solution was found to be 58 per cent.

* Daeschner, D. R. P. 124,980, Kl. 23 b.

4. **Sulpho-acids.** 20 c.c. of the solution obtained in (3) were titrated in the presence of phenolphthalein with $N/10$ sodium hydroxide. The total amount of acid, calculated as sulphuric acid, including free sulphuric acid and sulpho-acids, was 60.2 per cent. Since according to (3) only 58 per cent of sulphuric acid was present, 2.2 per cent must be due to the sulpho-acids, the molecular weight and actual amount of which were not determined, since this was unnecessary in this case.

5. **Water.** Water was present in considerable amount, as shown by a distillation of the original sample at 120°. 14 per cent of an aqueous distillate (water plus sulphurous acid) distilled; however more than this must have been present since a considerable portion was retained by the sulphuric acid.

6. **Other Components.** After evaporation of 100 c.c. of the aqueous solution obtained in (3) and driving off the sulphuric acid, there remained besides traces of organic substances about 1 per cent of iron oxide (referred to the original sample).

7. **Résumé.** The sample was not an acid resin but was a spent acid from the mineral oil refining process, containing about 58 per cent of sulphuric acid, about 19 per cent of acid resins insoluble in water as well as some water and water soluble materials.

(*d*) **Spent-lyes.** The waste lyes obtained by the neutralization of acidified oils are either thrown away or if it appears profitable, they are regenerated by calcination. Since these lyes contain, besides free alkali and salts of petroleum acids, at times considerable amounts of unchanged oils dissolved or emulsified, in some factories, by the addition of mineral acid or spent acid, dark colored "soap oils" are separated. These are added to other oils, for example, lubricating oils for wagons, etc.

TABLE 66

PROPERTIES OF NAPHTHENIC ACIDS FROM LYES OBTAINED IN THE REFINING OF LUBRICATING OILS

Acids from	External appearance	Saponification value	Iodine value		Reaction for sulphur
			Waller	Wijs	
Saponaphtha	Viscous, dark brown, odor of naphthenic acids	145 8	28 4	42 3	Faint
Russian lubricating oil	Thick oil, stringy, brown black, odor of naphthenic acids	118 3	5 5	21 8	Strong
Galician lubricating oil	Soft resinous, stringy, brown black, odor of naphthenic acids	87 6	30 7	51 5	Same
Rumanian lubricating oil	The same	157 4	4 0	....	Same

All acids in the above table* had the characteristic odor of naphthenic acids and were completely soluble in naphtha. The sulphur present points to sulpho-acids or alkyl-sulphuric acids.

Naphthenic acids from the main fractions of Baku petroleum were found† to show the properties tabulated below.

TABLE 67

PROPERTIES OF NAPHTHENIC ACIDS FROM RUSSIAN PETROLEUM

Naphthenic Acids from	Specific gravity at 15°	Acid value	Iodine value Hübl-Waller	Sulphur per cent	Engler degree		
					30°	50°	100°
Kerosene	0.9650	255	0.90	0.3	4.2	2.3	1.2
Light solar oil	0.9513	170	2.42		15.0	5.5	1.6
Heavy solar oil	0.9418	136	2.5		19.0	6.2	1.7
Spindle oil	0.9358	103	6.17		34.8	10.1	1.9
Machine oil	0.9350	87.5	7.18		47.7	13.3	2.1
Cylinder oil	0.9294	32.6	11.4		97.9	23.8	2.7

To determine the advisability of recovering the by-products, the spent lye is examined for alkalinity, content of neutral soaps and yield of " soap oils. "

Two naphthenic acids of high molecular weight have been obtained from Baku petroleum; one, of formula, $C_{19}H_{37}COOH$, has the boiling point 310 to 320°, the other has the composition $C_{24}H_{47}COOH$. Their purification was accomplished by a fractional precipitation of their silver salts.

In washing the ether solution of the acids with water, the acids in part pass into the aqueous layer, giving it a brown color. This difficulty is overcome by washing with concentrated solutions of sodium sulphate. Lidoff ‡ determined the iodine number of the naphthenic acids from the lyes obtained in the preparation of kerosene and found values from 1.4 to 3.9, the acid values being 213.9 to 238.9. Oils containing naphthenic acids gelatinize in the Lux test for saponifiable fat, without showing any foaming; this may easily lead to the incorrect assumption of the presence of saponifiable fat.

Bauer§ claims that naphthenic acids can be separated from their

* Mitteilungen, **27**, 17 (1909).

† Petroleum, **9**, 1373 (1913). Z. angewandte Chem., **27**, I, 407 (1914).

‡ Chem. Rev., **9**, 134 (1902).

§ D. R. P. 302210. Kl. 12°.

impurities (as mineral oil) by the solubility of the former in anilin. Holde states that fatty oils and fatty acids, pine-tar oils and others are also soluble in anilin; mineral oils are insoluble. Mineral oil mixed with fatty oils is more soluble in anilin.

CHAPTER III

NATURAL ASPHALT

I. General

According to Engler the asphalts are derived from petroleum hydrocarbons through polymerization, free oxygen acting as a catalyzer of the change. It has been shown experimentally that the formation of asphalt takes place much more rapidly in the presence of air, yet the amount of oxygen absorbed is too small to explain the formation of the asphalt through oxidation.

The oldest known source of asphalt is the Dead Sea, on the shores and surface of which asphalt is obtained in large quantities, especially after earthquakes. Recently the asphalt deposits of the island of Trinidad have attained a far greater prominence because of the more favorable conditions for working the deposit and shipping the product. The Syrian asphalt contains very little ash, gilsonite containing only 0.5 per cent, while Trinidad asphalt may contain 33 to 54 per cent of mineral components.

The Trinidad and Bermudez asphalts are much used for street paving. According to Richardson* the crude Trinidad asphalt contains from 28 to 30 per cent of water; in the dry condition, 56 per cent of bitumen and 38 per cent of mineral components, the rest being hydrate water of the clay and insoluble organic matter. The pure bitumen softens at 76° and melts at 83°, has a specific gravity of 1.032 at 25°, contains 82.33 per cent carbon, 10.69 of hydrogen, 6.16 of sulphur and 0.81 per cent of nitrogen. The similarly constituted Bermudez asphalt contains from 11 to 46 per cent of water; in the dry condition, 95 per cent is bitumen, containing 82.88 per cent carbon, 10.79 hydrogen, 5.87 sulphur and 0.75 per cent of nitrogen.

Deposits of asphalt have been discovered also in Mexico, California, Utah and Colorado.

The external appearance of the asphalts varies considerably; some are hard, brittle and black; others, soft and viscous in nature (mineral tar or "goudron minéral"). In several instances this mineral tar has penetrated and saturated porous rocks, particularly limestone. Such bituminous limestone is found in France (Val Travers, Seyssel

Petrol., 7, 1347 (1912).

in the Rhone valley), in Italy (San Valentino), in Sicily, in Dalmatia (Ragusa), in Alsace, in Hannover (Limmer). The asphalt rock mined by the asphalt company, San Valentino, Reh & Co., has the following composition:

Asphalt Rock	Per cent
Bitumen	10 7 to 15 7
Insoluble silica	0 1 to 0 5
Soluble silica	Traces
Calcium carbonate	50 to 86
Magnesium carbonate	1 to 32
Iron oxide and aluminum oxide	0 2 to 1 2
Moisture and matter volatile at 100°.	0.1 to 1.0

II. Chemical Nature of Asphalt

Richardson distinguishes between the following components of natural asphalt: petrolenes, malthenes, asphaltenes, and carbenes. Petrolenes are the hydrocarbons volatile at 325° F.; malthenes are non-volatile hydrocarbons, soluble in naphtha; asphaltenes are insoluble in naphtha, but soluble in cold carbon tetrachloride; carbenes are insoluble in cold carbon tetrachloride but dissolve in carbon disulphide. Graefe has shown* that these are not clearly defined groups but probably represent stages in development, as is indicated by the fact that asphaltenes, malthenes, and carbenes may change into each other under the influence of oxygen or sulphur.

Furthermore the above classification does not take into consideration the recently discovered saponifiable components; Marcusson† distinguishes between the following components of the asphalt bitumen: unchanged oil, resins, asphaltenes, asphaltic acids and anhydrides of the latter.

To isolate the acid components a benzol solution of the asphalt is treated with alcohol to precipitate pitch-like material, the solution titrated with $\frac{N}{10}$ alkali and the dissolved unsaponifiable material extracted from the soap solution by the method of Spitz and Hönig (page 197); the asphaltic acids are separated from the soap solution in the usual manner. The unsaponifiable matter obtained by the method of Spitz and Hönig, as well as the pitch-like material, obtained from the benzol solution on adding alcohol, are saponified with normal alkali, and again the acids set free; the acids present as anhydrides are thus obtained. The material not reacting with alkali is treated in benzol solution with an excess of naphtha

* Z. angewandte Chem., **26**, 527 (1913).

† Z. angewandte Chem., **29**, 346, 349 (1916).

to separate the asphaltenes. The naphtha solution is concentrated, the residue mixed with fuller's earth and then extracted with low boiling " benzine " (50°) in a Soxhlet apparatus; the unchanged oil is brought into solution by this operation. The resins are extracted from the fuller's earth with chloroform.

Values obtained on examination of Trinidad and Bermudez asphalt are given in the following table:

TABLE 68

NATURAL ASPHALTS

Bitumen from	Free asphaltic acids per cent	Anhydrides of asphaltic acids per cent	Asphaltenes per cent	Resins per cent	Unchanged oily portion per cent
Trinidad	6 4	3 9	37 0	23 0	31.0
Bermudez	3 5	2.0	35 3	14 4	39.6

The oily components show the same properties as mineral oils; they are mainly saturated in nature (iodine value 16 to 18); the unsaturated portion gives in part the formolite reaction (page 110); small amounts of oxygen-, sulphur-, and nitrogen- containing components are present; less than 1 per cent of paraffin is found (see page 271).

The resins (page 185) are like those obtained from mineral oils, being solid, red brown to brown black, melting under 100°, and little soluble in acetone. With fuming nitric acid they give at − 10° light brown iso-nitro-derivatives, on warming with concentrated sulphuric acid at 100° they are changed into derivatives insoluble in water; as they contain organic sulphides, they react with mercuric bromide in ether solution, forming insoluble bodies.

Asphaltenes form on prolonged heating of mineral oils or of petroleum resins or even on standing of darker oils (page 108); asphaltenes are dark brown to black, powdery, and swell on heating, but do not melt; they are almost insoluble in alcohol or naphtha, and contain considerable sulphur. The sulphur compounds determine the light-sensitiveness. The asphaltenes behave with reagents very much as do the resins. Absorption of iodine and bromine by resins and asphaltenes is not to be ascribed to an unsaturated nature; probably substitution takes place, and halogen is held by the sulphur-, and oxygen- containing components with the formation of sulphonium and oxonium derivatives. Both the resins and asphaltenes are saturated bodies.

The asphaltic acids, like the tars obtained on the resinification of mineral oils (page 188), are brown, of tarry consistency, somewhat resinous; they are insoluble in naphtha, but easily soluble in alcohol

and in chloroform. Their specific gravity is greater than one. They contain sulphur and form insoluble derivatives with mercuric bromide. Acids from Trinidad asphalt had an acid value of 98.5, saponification value of 120.4, an iodine alue of 22.4, and a sulphur content of 3.1 per cent. These materials, supposed to be dioxymonocarbonic acids, have a great tendency to form anhydrides; they have (opposite to naphthenic acids from petroleum) a high molecular weight and form copper salts insoluble in naphtha.

When Tartaro asphalt is treated with alkaline water (page 283) "resin acids" are obtained which can be precipitated by acetic acid and lead acetate; they are partially soluble in water as well as in boiling alcohol, are difficultly saponifiable with caustic potash, and melt at 47.5°

III. Asphaltites

The asphaltites* represent a special class of natural asphalts; to these belong the so-called "glance pitch," grahamite, and gilsonite. They do not occur on the surface of the earth, as do the natural asphalts, but occur in true veins; they are used in the preparation of asphalt varnish.

Asphaltites have considerable lustre, are hard and brittle and are easily pulverizable. They contain no free acid (the acid value being only 0.1 to 0.5, only manjak from Barbadoes showing 2.4); the saponifiable materials are present as anhydrides. Richardson states that asphaltites contain a high percentage of carbenes (grahamite) or coke-like components (albertite). The amount of mineral material in asphaltites is small; they contain less than 7 per cent (manjak 17 per cent) of oily components resistant to sulphuric acid. These are liquid at 20° and almost free from paraffin; brittle, pulverizable petroleum residues contain more than 20 per cent of oily material, (not liquid at 20°, and containing more than 2 per cent of paraffin). Asphalts contain at least 17 per cent of oil.

IV. Extraction and Treatment

The asphalt is obtained from the Trinidad and Bermudez deposits by surface working; other deposits of asphalt and the bituminous limestones are mined. Near the asphalt lakes, liquid asphalt oozes out of springs and craters and hardens in the air.

Since the naturally occurring asphalt contains earthy impurities which increase the cost of transport, in many cases it is purified at

* Chemiker Zeitung, 38, 822 (1914).

the source of supply by melting or by distillation to increase the content of bitumen. The "Trinidad epuré" has been somewhat purified by melting. By this process a part of the asphalt is destroyed by overheating because of which the poorer qualities may contain a considerable amount (up to 11 per cent) of free carbon.*

In the case of asphalt from Tataros (Hungary), the melting out of the asphalt must, according to H. J. Jachzel, be performed in the presence of faintly alkaline water in order to dissolve the resin acids and thus allow the separation of asphalt and sand. After being stored in the air, the asphalt from Derna (Hungary) also requires alkaline water to separate it from the sand. The absorption of oxygen is accompanied by an increase in weight and in hardness of the asphalt.

Distillates from this Hungarian asphalt showed the following properties:

Carbon	from 87 0	to 87 5	per cent
Hydrogen	" 12 2	to 12 3	"
Oxygen	" 0.0	to 0.5	"
Nitrogen	traces only		
Sulphur	" 0.20	to 0 29	"
Specific gravity	" 0 926	to 0 937	"
Engler viscosity at 20°	" 18	to 30 6	"
at 50°	" 3 4	to 4.5	"
Iodine value	" 20	to 30	"
Alcohol solubility	" 20	to 30	"

These indications point to the presence of practically pure hydrocarbons in these oils

TABLE 69

Material	Ash, per cent	Sulphur, per cent	Oily parts obtained according to Marcusson-Eickmann, per cent	Paraffin content of the oily parts, per cent	Acid values of the crack-distillates	
					I Distillate	II Distillate
Mexican asphalt	None	5.8	35	2.8	1.6	0 9
Goudron from Derna (sand melted out)	5.4	0.7	52	.....	3 4	2.6
Asphalt from Derna (sand melted out, and thickened)	6.0	0.9	25	1.6	0.7	0.7

* Lindenberg, Asphalt-Industrie, 11.

Recently there have come on the market residues obtained in the distillation of natural bitumens from America and from Italy; these have also been called "natural asphalts" (San Valentino-bitumen, Mexican asphalt, Venezuelan (Orinoco) asphalt and certain varieties of Cuban asphalt).

The intermediate position which the thickened natural asphalts occupy between natural asphalt and petroleum residues is shown in Table 69 which gives the results of recent experiments of Marcusson.

Natural asphalt is used in the preparation of varnish, in the rubber industry, in the preparation of insulating material and in the building industry.

The following brief account gives an idea of how Trinidad and Sicilian asphalt is worked up into compressed asphalt for German street pavements, asphalt mastic, tiles from rock asphalt mastic, waterproofing material, etc., at the works of the A.-G. Johannes Jeserich, Charlottenburg.

The raw material for the asphalt mastic is the crude Trinidad asphalt which is brought to the factory in irregular pieces. The asphalt is first purified by heating in a large tank with a large opening at the top; the mass is stirred mechanically and heated until the water contained, as well as other volatile matter, has escaped, the stirring facilitating the removal of the water and preventing the settling to the bottom of the fine clayey particles. The material thus obtained is allowed to run out from an opening at the bottom, through a trough over a coarse sieve (with 1 cm. mesh), to separate larger impurities, like pieces of wood, etc.

The asphalt thus obtained is mixed in similar vessels (provided with mechanical stirring devices) with powdered Sicilian asphalt and other materials (fluxes) for the preparation of asphalt mastic, waterproofing material, etc. Trinidad asphalt mixed with fluxes like mineral oil gives the so-called Trinidad goudron; this is added to the Sicilian asphalt rock powder with some sand to give it the properties of asphalt mastic. In the less valuable kinds of asphalt mastic, broken pieces of old pavements are added. The mastic used for filling the cracks of stone pavements, etc., may be made from less valuable materials, for example, coal-tar pitch, mixed with natural asphalt.

The compressed asphalt for laying compressed asphalt pavements is made from pure Sicilian asphalt rock, which has a brown color, with a dark-brown fracture, with a dirty white appearance when cut, and which contains 10 to 12 per cent of bitumen. The rock is broken up in special machines, powdered in disintegrators, transferred from these to the drying bins and is then ready for use.

The natural asphalt rock has the very important property of falling to a powder on heating; this powder can be again converted into a mass of the same hardness as the original rock by heating and pressing. Granular limestone artificially impregnated with bitumen is said, according to the results in practice, not to possess this property and after heating does not again become sufficiently hard under pressure.*

* Die Asphaltbaumaterialien usw., Normalverordnungsblatt für das K. und K. Heer, Wien, 1910.

The blocks or tiles of asphalt mastic are only a convenient form in which the mastic may be transported.

In the United States the pavements are not made with compressed asphalt; a natural asphalt rock is lacking, so that a mixture of sand and rock powder (diabase, etc.), with Trinidad or Bermudez asphalt and fluxes, is used.

V. Differentiation of Natural Asphalt and Petroleum Pitch

Since the sulphur content of natural asphalt varies considerably, it is possible to prepare mixtures with petroleum pitch, the sulphur content of which lies within the normal limits for natural asphalt. According to Malencovic* the natural asphalts will, the sulphurized petroleum pitches will not, give a precipitate with mercuric bromide in ether solution; the test has, however, not been found useful for the detection of natural asphalt in the presence of petroleum pitch, but has found application in the detection of natural asphalt or petroleum pitch in fat-pitch (see page 265).

Natural asphalt and petroleum pitch differ very slightly in elementary composition; the differences, however, become much more pronounced if (according to Holde and Eickmann), instead of examining the pitches, the extracts obtained with various solvents are analyzed.

Different pitches are melted up with sand and bone-black to a pulverable mass and then successively extracted in a Graefe extraction apparatus (Fig. 64, page 107) with petroleum ether, petroleum naphtha (sp. gr. 0.70), benzol and chloroform. (See Table 70.) The consistency of the extracts passes from a thick oily condition to a hard resinous material like colophony, the color becoming darker and the odor disappearing. In the extracts obtained from petroleum pitch, the oxygen content increases at the expense of the hydrogen, the amount of carbon remaining constant. In the natural asphalts, however, the amount of sulphur and oxygen increases decidedly (with the exception of the oxygen content of No. 3), while the carbon content decreases and the hydrogen remains constant.

See page 270 for further methods used in distinguishing between natural asphalt and petroleum-pitch.

VI. Quantitative Determination of Natural Asphalt in the Presence of Coal-tar Pitch

Mixtures of natural asphalt and coal-tar pitch are much used for making asphalt cements, for waterproofing of masonry, etc. Since such cements should contain at least 25 per cent of natural asphalt,

* Baumaterialen, **1906**, 29.

TABLE

ELEMENTARY ANALYSES OF THE

Material	Sample	Source	Ash, %	Melting point of the total bitumen extracted with chloroform	Bitumen soluble in petroleum ether													
					Bitumen remaining in solution (soft resinous stringy)							Separating on standing cold (brittle)						
					Amount %	% C	% H	% S	% N	% O	% Ash	Amount %	% C	% H	% S	% N	% O	% Ash
Natural asphalt	1	San Valentino	15	95	40.4	84.9	7.5	5.8	*	1.8	0	1.0	78.6	8.8	8.3	*	4.3	.
	2	Trinidad epuré	40	91	66.5	83.3	10.8	2.3	0	2.6	0	0.3				*		..
	3	Trinidad	37	82	59.0	82.8	10.2	3.6	0	3.4	0							..
Petroleum pitch	1	Galician	0	69	70	87.7	10.4	0.9	0	1.0	0	8.7	88.9	7.2	1.4	*	2.5	0
	2	"	0	91	54.1	87.0	10.3	0.7	*	2.0	0	4.2	88.0	7.4	1.4	*	3.2	0
	3	"	3.2	43.3	78.9	86.2	10.6	0.5	*	2.7	0.5	3.0	86.6	7.4	1.3	*	4.7	0
	4	Russian	0.2	27	85.5	86.02	11.98	1.48		0.52	0							....
	5	"		17.8	89.0	..	.											....
	6	German		24.0	75.0		..											....

* Trace

an approximately quantitative determination is of value. According to Marcusson* this can be made by changing the coal-tar pitch into water-soluble materials by heating with concentrated sulphuric acid, while the amount of water-insoluble materials remaining after treatment with sulphuric acid gives an idea as to the amount of natural bitumens present. The determination is made as follows:

10 grams of the sample are treated with 75 c.c. of ether-hydrochloric acid (as in the determination of bitumen by the method of Prettner, see page 273) in 3 or 4 portions, stirring constantly.† After stirring ten minutes, an equal volume of

* Zeit. f. angew. Chem., **26**, 91 (1913).

† The bitumen cannot be quantitatively extracted with benzol and chloroform, since the carbonaceous particles in the coal-tar pitch adsorb a small part of the bitumen, which is given up to the solvent only with difficulty.

70

Components of Asphalts

Bitumen insoluble in petroleum ether but soluble in naphtha (in 1 soft, in the others, brittle)							Bitumen insoluble in naphtha, soluble in benzol (brittle)							Bitumen insoluble in benzol, soluble in chloroform (brittle)						
Amount %	% C	% H	% S	% N	% O	% Ash	Amount %	% C	% H	% S	% N	% O	% Ash	Amount %	% C	% H	% S	% N	% O	% Ash
22 5	81 5	9 6	7 1	*	1 7	0	13 8	79 7	7 6	8 2	*	4 5	0	4 2	76 3	7 6	9 6	0	6 5	0
2 6	81 0	9 8		*		0 7	27 3	74 7	7 8	7 2	*	10 3	0	3 0	74 7	8 5	7 5	*	9 3	0
3 3	77 0	7 8	4 7 1 0	*	5 7	0 9	19 6	80 2	8 5	4 7	*	5 7	0	3 0	80 8	9 1	7 5	*	2 0	0.6
0 7	.			*			17 1	90 2	6 3	1 4	*	2 1	0	1 1	88 8	6 0	1 0	*	4 2	0
3 6	86 0	7 4	1 2	*	5 4	0	20 8	88 5	8 4	0 9	*	2 2	0	0 6	89 1	6 1		*	< 4 8	0
1 0	81 8	9 6		*		0	1 4	85 9	5 9	1 4	*	6 8		1 5	87 0	6 0	1 6	*	4 8	0
2 4							9 8	89 31	8 54	0 62		1 18	0 35	0 8					.	......
1 0							5 5	89 93	7 02	1 09		1 15	0 45	0 8		.			.	......
2 0	85 8	8 85				0	12 0	88 15	7 44				0 13	4 6	83 36	5 97	1 71		8 1	0.86

* Trace

water is added and the mixture heated on a steam bath till the odor of ether disappears. The insoluble matter is separated by filtration, washed free from acid, and after drying the paper, the bitumen determined by extraction with boiling chloroform in a Graefe extraction apparatus (Fig. 64, page 107). By evaporating the chloroform, the bitumen to be sulphonated is obtained, its quantity being determined by drying at 105°.

3 grams of this bitumen are heated in a thick walled test tube with 6 c.c. of conc. sulphuric acid (on a boiling water bath) with frequent stirring for ¾ hour. When the sulphonation is finished, the reaction product is cooled and poured into 200 c.c. of water in an Erlenmeyer flask. In the course of an hour, there will collect at the bottom of the flask a black, powdery, somewhat crumbly precipitate.

The filtration of the precipitate causes trouble at times, since the filter becomes easily clogged. It is advisable to use a Buchner funnel of 7 cm. diameter and a weighed hardened filter. The liquid is decanted upon the paper without stirring up the precipitate, covering the paper with only a thin layer of liquid and filtering at first without suction. The precipitate in the flask is at first washed with water

by decantation and only transferred to the funnel at the end.* Lumps are broken up with a glass rod. The washing is continued till the filtrate no longer reddens methyl orange. The precipitate and paper are then dried at 105°. The weight obtained is recalculated to the original weight of material and an empirically determined correction of 4 per cent is added.

As Marcusson has shown for mixtures of coal-tar pitch with 15 to 60 per cent of crude Trinidad asphalt or with Trinidad epurè, this method gives results accurate to within 1.5 per cent. It must, however, be remembered that in this way only the amount of natural asphalt bitumen is determined; the actual amount of natural asphalt present depends upon the amount of mineral matter present (page 279). A direct determination of the ash may be misleading since it is easy to add mineral matter.

VII. German Specifications for Asphalt

Because of the tremendous confusion in the nomenclature of asphalt materials the following definitions and specifications have been suggested by a number of interested German organizations.†

Compressed asphalt may be either natural or artificial. The former includes also the German asphalt meal prepared by enriching bituminous rock with a flux (gudron). A mixture of sand and bitumen is considered artificial. The natural asphalt should contain from 8 to 13 per cent of bitumen and the rest should be mineral matter (mostly $CaCO_3$, but 8 per cent of $MgCO_3$, 5 per cent of clay, 2 per cent of quartz, 0.8 per cent of gypsum and 0.5 per cent of pyrite may be present). It should all pass a 2 mm. sieve and most of it a 0.63 mm. sieve. No pitch or tar-pitch must be present, but petroleum residues or paraffin oil may be added to the German asphalt. The melting point (Kraemer-Sarnow) must be above 28°, the solidification point‡ below 10°. Not more than 1 per cent of organic matter (other than bitumen soluble in chloroform) must be present; a larger amount indicates overheating of the meal. The density§ should lie between 1.7 and 2.2; hydraulic pressure may however produce a density of 2.2. The water absorption in partial vacuum should be less than 14 per cent by weight, equivalent to 25 volume per cent. After 28 days in water it must not swell more than 5 per cent (German meal not over 15 per cent).

Artificial compressed asphalt should contain 9 to 12 per cent of bitumen, and the rest should be mineral matter (stone-dust and sand). Cement must not be present. 90 per cent should pass a 0.63 mm. sieve. The bitumen should be natural asphalt or petroleum residue (of asphaltic crude). Tar and tar-pitches not allowed.

* If a centrifuge is available, this will make the separation of the precipitate from the supernatant liquid an easy matter.

† Marcusson, Mitteilungen, **34**, 40 (1916). Petroleum, **12**, 921 (1916).

‡ By dipping a thermometer bulb in the warmed bitumen, then cooling in a freezing mixture, the layer must be so hard that it cannot be scratched with the finger nail.

§ Schmidt-Hermann "Die Prufung von Stampfasphalt," Berlin, 1915, page 17.

Melting point over 38°. Insoluble organic material not more than 1 per cent. Density must be over 2. Other conditions much as for the natural asphalt.

Gudron (flux) must contain Trinidad asphalt to which has been added crude oil, natural mineral pitch or paraffin oil to give the desired consistency, (for Grade I) or to get a second grade product Trinidad asphalt may be mixed with petroleum residue free from paraffin (Grade II). Tar-gudron may contain residues from lignite- and coal-tar distillation or other pitches also. Grade I should contain 60 per cent, Grade II 80 per cent bitumen. Tar-gudron will in general not contain any mineral material; but not more than 21 per cent of carbonaceous material (insoluble in toluol) should be present. The melting point of Grade I must be over 38°, of Grade II, over 28°.

Asphalt mastic should contain at least 15 per cent of bitumen, the rest mineral matter (mostly $CaCO_3$). Nearly all should pass a 0.63 mm. sieve. No tar or tar-pitch should be present. The material should be a mixture of bituminous rock and flux (gudron I or II). Melting point must be above 38°. A poorer grade tar-mastic consists of ground limestone (not over 80 per cent) and tar-gudron. Not over 21 per cent of insoluble carbonaceous material should be present.

For a surface mixture for streets a "compound" of asphalt mastic with Trinidad-gudron, sand and rock dust is used. From 8 to 13 per cent of bitumen, the rest mineral matter ($CaCO_3$, quartz, basalt, granite, graywacke, greenstone), should be present, but no tar or tar-pitch. Melting point over 38°. Density, from 2.2 to 2.45.

For use in filling the spaces between paving blocks and for joining in a tight manner clay drain pipes, asphalt cement should contain from 30 to 50 per cent of mineral matter (unburned clay, marl, infusorial earth or limestone) which has been ground so fine that 95 per cent passes a sieve of 900 meshes per sq. cm. and 75 per cent one of 5000 meshes. The bitumen may be asphalt, petroleum, or tar bitumen, or a mixture, but must not contain more than 16 per cent of carbonaceous insoluble material. Melting point should be over 28° and solidification point below -10 for pavements and $+5°$ for pipes.

For protecting masonry there may be used a material containing not more than 40 per cent of mineral matter. The bitumen may be derived from asphalt, petroleum or tar and must be resistant to 5 per cent solutions of hydrochloric acid, sulphuric acid and caustic potash. It must not allow passage of water.

For roofing paper and felt and for tar paper in general, the bitumen must resist passage of water, and must not absorb water. It should not cause brittleness in the paper on heating and it must not volatilize more than 0.4 per cent on heating to 50° for 5 hours.

CHAPTER IV

Ozocerite (Earth Wax)

I. Occurrence

Crude ozocerite is mined principally at Boryslaw, Starunia and Dzwiniacz in Galicia. Deposits have recently been found in Texas which yield a product* of melting point 75°, of specific gravity 0.9127, and refractive index 1.442; a deposit occurring in Utah has not yet been developed commercially. In the crude state ozocerite has a dark brown to greenish black color, and a waxy consistency; it occurs at times in leafy masses (" aderwax ") with only a faint odor, but may have an odor suggesting that of crude petroleum. The melting point of different samples ranges from below 60° for the poorer grades, to from 68 to 75° for ordinary varieties, while the best grade (" marble wax ") may melt as high as 84°. Recently it has been possible to obtain ozocerite directly from crude oil by cooling a naphtha solution of the oil.

Formerly it was supposed that ozocerite was a precursor of petroleum but now it is assumed† that solid and liquid hydrocarbons were formed simultaneously from the same raw material (fatty and waxy residues; oleic acid and other liquid material producing liquid hydrocarbons, solid fatty acids producing paraffins). Under the pressure of the strata above, or by gas pressure, the crude petroleum continuing amorphous and crystalline paraffin was forced higher, through fissures and through porous materials in the earth, whereby the paraffin separated from the more rapidly moving crude oil. In this way a separation of crystalline and amorphous paraffin was brought about, since the former exhibits a greater solubility and therefore is carried along more readily by the crude petroleum than the undissolved, essentially amorphous paraffin. By the filtration of the paraffin through porous rock, the resinous and colored components of the paraffin were removed, producing the pale yellow to brown " ader wax;" where the impurities left in the porous rock were increased in concentration, a darker and smeary " lep wax " was produced. In the deposits of ozo-

* Chem. Umschau, **24**, 39 (1917). See also Muck, Erdwachsbergbau in Boryslaw, Berlin, 1903.

† Marcusson and Schlüter, Chemiker Zeitung, **38**, 73 (1914).

cerite is also found the material called "kindebal" which is intermediate in composition between petroleum and ozocerite; this material is similar to the deposit* forming as a dark-colored, soft waxy mass in pipe-lines. The optical properties also point to a connection between ozocerite and petroleum, the solid components being inactive, the liquid portions dextro-rotatory as in petroleum. Material similar to ozocerite has been found at times in cylinder oils and in the above-mentioned deposit separating in pipes of pipe-lines.

II. Chemical Nature

It was formerly supposed that paraffin consisted of a mixture of the lower members of the series of saturated hydrocarbons, while ceresine contained the members of high molecular weight; it has been shown† that the crystallizable paraffin contains straight-chain hydrocarbons while ceresine contains forked-chain bodies. Ceresine shows a higher specific gravity than does paraffin of the same melting point, greater index of refraction and higher molecular weight, as well as greater viscosity when melted.

Ceresine reacts with fuming sulphuric acid when warmed on a water bath with production of carbonaceous material, while paraffin is hardly attacked. On contact with chlorsulphonic acid, hydrogen chloride is vigorously evolved.

Naphthenic acids are probably not present, for after treatment with $KMnO_4$ in pyridin solution, the residue has the same refractive index as the original ceresine; naphthenic acids would have succumbed to this method of attack. Concentrated nitric acid forms no nitro-bodies indicating naphthenic acids; the products are like those from paraffin.

On destructive distillation of ceresine it decomposes into paraffin hydrocarbons of lower molecular weight and lower melting point, liquid olefins, and paraffin hydrocarbons; this seems to point to the presence of forked-chain hydrocarbons.

Lower-melting ozocerites contain small amounts of crystalline paraffin components. In all crude ozocerites are found oxidized, dark colored bodies as impurities.

* Ding. Poly. Journ., **284**, 143, 153, 252, 396, (1892). Mitteilungen, **21**, 58 (1903). Chem. Ztg., **38**, 73 (1914).

† Chem. Ztg., **39**, 613 (1915). Mitteilungen, **33**, 415 (1915).

III. Preparation of Ceresine

The crude ozocerite is freed from the coloring matter by heating with 20 per cent of concentrated sulphuric acid at 120°, gradually increasing the temperature to 200°, about 20 per cent of the wax being lost by this operation. The acid material is purified by means of the carbonaceous residues from the manufacture of yellow prussiate of potash, a natural yellow wax (ceresine) being obtained. By repeated purification in which the residues are separated from the purified ozocerite in filter presses (warmed up) and the ceresine remaining in the charcoal extracted with naphtha, there is finally obtained a white product, the value of which depends on its color and the height of its melting point.

IV. Examination

(a) *Testing the Crude Ozocerite for its Yield of Ceresine*

The yield of refining is determined, according to Lach and v. Boyen,* by heating 5 grams of crude wax with 18 per cent (0.45 c.c.) of conc. sulphuric acid to about 200° till all odor of sulphur dioxide is gone. Into the hot mass is then stirred 10 per cent of animal charcoal or (yellow prussiate residues, dried at 140°) and about 6 grams of extracted sawdust. The cooled mass is extracted in a Graefe extraction apparatus (page 107) with naphtha. The amount of extract gives the yield. With high melting ozocerites, high boiling naphtha must be used to shorten the time of extraction. The yield depends on the amount of oil destroyed, and the amount of ceresine unattacked by concentrated sulphuric acid.

(b) *Examination of Ozocerite and Ceresine for Foreign Bodies*

Ozocerite and ceresine are used industrially in the manufacture of candles, in cable insulation, in shoe, stove and floor polishes and for other purposes; they are expensive and are often adulterated with paraffin. This adulterant is the cheapest and, therefore, the most profitable and is not easily detected when present in small amounts.

For some time ozocerite has been refined mixed with paraffin, such mixtures being known on the market as "ceresine," while the product obtained by the refining of pure ozocerite is called "pure, refined ozocerite." In this book the original definition of ceresine as pure refined ozocerite is retained.

1. **Paraffin.** This is tested for in the refined material, as the dark, resinous and oily components of the crude ozocerite would interfere

* Zeit. f. angew. Chem., **11**, 383 (1988).

with the tests, which are mostly optical. The skilled manufacturer estimates the purity of the ceresine by noting its waxy, amorphous structure, and its ring.

If ozocerite is to be tested, it is first refined with conc. sulphuric acid and 1 gram of the purified material dissolved in chloroform (50 c.c.), warming gently; 18 c.c. of absolute alcohol are then added to the solution cooled to + 20°, the ceresine separating in an amorphous condition and being collected on a filter plate by suction. To the filtrate are then added, 40 c.c. of absolute alcohol at 20°; after standing, the precipitate is collected by suction, the paraffin precipitate showing a crystalline structure. Taken alone this test is unsatisfactory.

(α) The specific gravity of paraffin (solidification point 44 to 58°) is 0.867 to 0.915 at 15°, of ceresine (solidification point 56 to 84°) between 0.912 and 0.943. These differences allow the detection of larger additions of paraffin.

(β) The index of refraction expressed as scale divisions of the butyro-refractometer gives a much better test for paraffin in ceresine, as was shown by Ulzer and Sommer.* Since the differences between ceresine and paraffin are not large, these investigators determined the refractive index of an alcoholic extract because the more soluble paraffin collects in the alcohol.

In order to become independent of the variations of the refractive index of pure ceresine in testing for paraffin, Marcusson and Schulter† fractionally precipitated ceresine, pure and mixed with paraffin, with a liquid first used by Graefe for the qualitative detection of ceresine in paraffin (for 3 grams of ceresine, 30 c.c. of carbon disulphide and 300 c.c. of alcohol-ether, 1 : 1, alcohol 96 per cent). On the basis of these observations, they suggested a qualitative, and with the aid of the values a quantitative, estimation of the paraffin, thus much facilitating the testing of ceresine. Since, however, ozokerites of abnormal precipitation values were possible, they promised a further examination of the method.

Holde studied anew the detection of paraffin in ceresine using another solvent and precipitant.

With Landsberger he devised a method in which a chloroform solution of the ceresine is treated with alcohol, a precipitate being produced; a fractionation is thus effected as can be shown by refractometric tests. Holde and Franck‡ showed that low melting paraffin (41.5 to 42°) had a refractive§ index (n) at 90° of − 7.2, normal hard paraffin (50

* Chem. Ztg., **30,** 142 (1906).

† Chem. Ztg., **31,** 348 (1907); **39,** 613 (1915).

‡ Petroleum, **9,** 671 (1914).

§ Determined at 100° in Abbe refractometer by heating with steam, adding 0.004 to recalculate to 90°, then using Table 10 to convert to degrees on the butyro-refractometer.

to 51°) values from − 0.4 to + 1.5, and higher melting paraffins (60 to 68.8°) refractive indices ranging from + 3.0 to + 6.5. All industrial samples of melting point up to 61.5° contained from 0.1 to 0.2 per cent of non-precipitable oil of refractive index at 90° ranging from 22 to 38. Holde and Smelkus found the refractive index of ceresines to range from 7.6 to 19.2; highly refined material gave values 10.1 to 1 (Tscheleken ceresine gave 19.2).

The following method is suggested. 2 grams of ceresine (or the same amount of ozocerite) is dissolved in 60 c.c. of chloroform by heating gently in a 200 c.c. Erlenmeyer flask, avoiding boiling. After cooling to 20°, 120 c.c. of (96 per cent) alcohol are added, the mixture being kept at this temperature for 20 minutes. The precipitate is then collected by suction on a Buchner funnel (precipitate I). The filtrate is freed from solvent by distillation, the last portions being evaporated from the open flask; this residue is dissolved in 10 c.c. of chloroform, brought to 20° and precipitated with 30 c.c. of (96 per cent) alcohol. After 20 minutes, the precipitate is collected as before (precipitate II). The filtrate is freed from solvent by evaporation in a small tared vessel (non-precipitable residue "a"). After determining the weight and refractive index of the residue "a," it is redissolved in 5 c.c. chloroform and reprecipitated with 30 c.c. of alcohol, thereby obtaining a precipitate III and on evaporation — "residue b."

The precipitates, I, II, and III, and the residues (a) and (b) are weighed, and their refractive indices determined on the Zeiss-Abbe refractometer, the values being recalculated to scale divisions on the butyro-refractometer. The results are tabulated as in Table 71.

TABLE 71

REFRACTIVE INDICES OF CERESINE AND CERESINE-PARAFFIN MIXTURES AFTER FRACTIONAL PRECIPITATION

	Precipitate I		Precipitate II		Residue (a)		Precipitate III		Residue (b)	
	per cent	n_{90}	per cent	n_{90}	per cent	n_{90}	per cent	n_{90}	per cent	n_{90}
Pure ceresine	76.7 to 93	8.7 to 17.9	1.5 to 11.4	3.8 to 14.1	3.3 to 8.4	13.6 to 31.2	0.4 to 1.3	2.7 to 8.9	2.1 to 7	17.2 to 33.9
Ceresine + 10 per cent paraffin	71.5 to 84.5	8.6 to 17.5	5.6 to 14.4	2 to 5	5.3 to 9.7	4.5 to 16.8	0.8 to 2.1	−0.1 to 3.3	3.6 to 8.2	6.2 to 20.3
Ceresine + 15 per cent paraffin	75.4	13.3	9.3	3.6	11.7	14.6	2.5	1.1	8.5	18
Ceresine + 20 per cent paraffin	75.5	12.4	9.7	2	11.5	11.5	2.1	−0.1	8.7	15.4

An addition of 15 per cent of paraffin may be detected in precipitate II and more plainly in precipitate III. Ten per cent may be detected by means of a quotient obtained as follows: —

$$\frac{n_{III} + n_{(b)}}{w_{III} + w_{(b)}}$$

In this (n) is the refractive index and (w) is the weight of the fractions. This quotient of normal ceresine ranges from 3.3 to 8.1; with a 10 per cent admixture of paraffin the quotient is 1.3 to 2.6.

This refractometer method can be used for mixtures of normal ceresines and paraffins of various melting points, but not for artificial mixtures to which oil, or paraffin rich in oil, has been added. Such mixtures will be recognized by the considerable deviation of the observed refraction from the values for pure ceresine.

2. The amount of oil in ceresine is determined by adding to a chloroform solution of the sample at room temperature an equal volume of alcohol till the main mass of ceresine is precipitated; the precipitate is then separated and sucked dry, and in the filtrate the rest of the solid hydrocarbons precipitated according to page 108; the filtrate from this is evaporated and weighed.

3. Colophony is detected after exhaustive extraction with 70 per cent alcohol.

The alcohol is distilled from the combined filtered extracts, the residue dried at 100 to 115° (till just liquid) and then weighed. If fatty acids are also present, the alcoholic extract after evaporation of the solvent is further treated according to page 471. Colophony can be detected in paraffin by this method. See page 186 for reactions of colophony.

4. **Petroleum Residues,** that is, solid residues of mineral oil distillation, on treatment of the sample with petroleum naphtha, give heavy precipitates of asphalt which are easily soluble in benzol, and which, evaporated from such a solution, leave a black glistening asphaltic varnish; crude ozocerite is almost completely soluble in naphtha and gives only traces of residue (mechanical impurities).

5. **Mineral Additions** such as talc, kaolin, gypsum are examined by the regular analytical methods after ashing the sample; or, after solution of the ozocerite in naphtha, the residue is examined.

6. **Additions of Stearin, Palmitin, Japan Wax, etc.,** are detected by the methods described on page 380 and following.

7. **Melting Point, Solidification Point, Dripping Point** are determined as described (pages 36 and following).

CHAPTEP V

Hydrocarbons (Tars) Obtained by Distillation of Coal, Shale, Resins, and Wood

Petroleum, ozocerite and natural asphalt occur in the earth already formed; the so-called tars consist of hydrocarbon mixtures made by artificial processes, that is, destructive distillation of bituminous material, coal, shale, peat and wood, or are obtained as by-products of the gasification of the organic part of these materials.

A. Lignite Tar

I. General

Up to the time of the war lignite tar was obtained almost exclusively from the destructive distillation of bituminous brown coal, the residual coke being used as a fuel. During the war the increased demand for gaseous and liquid fuels and for lubricating oils led to the decomposition of lignite in gas producers at the lowest possible temperatures, whereby, in producing fuel and power gas, a tar rich in paraffin was obtained as a by-product.

The lignite tar and generator tar are separated by distillation, refining, refrigeration, and pressing into solar oil, cleaning oils, paraffin oils, or gas oils for motors, lubricating oils, paraffin and other products. About 50 per cent of gas oil is obtained from the tar.

The recovery and treatment of the generator-gas tar has not been highly developed as yet; the industry is in its infancy. There are obtained lighter oils and paraffin and good luricating oils of Engler degree 4.5 at 50°; different products are available depending on whether vacuum or steam distillation is used. The market is controlled at present by the products of the destructive distillation of lignite.

The destructive distillation industry, in the development of which Grotowsky, Schwartz, Riebeck, Wernecke, Krey and others took part, was made possible by the introduction of the Rolle upright cylinder for destructive distillation (1858). One of the most important advances of this industry was made when Wernecke* introduced the system of

Chemiker Zeitung, 37, 1560 (1913).

firing the retorts with the waste gases, thus saving an enormous amount of fuel. Later Krey used the gases in explosion motors.

The bitumen occurs in the lignite as a high melting material, the so-called montan wax (see page 528) which can be obtained industrially by extraction methods. Not every lignite is suitable for extraction however. Such lignites are destructively distilled and produce thereby a salve-like tar, formed by the decomposition of the montan wax, which tar is however less valuable (as are the oils obtained from it) than the high-melting montan wax. The yield of tar is greater than that of wax because bitumen which is not usually extracted under the conditions of operation is changed to tar on distillation.

Fritsch states that lignite is a transformation product of coniferous and deciduous trees of the tertiary period, while the waxes and resins found in lignite have been formed from vegetable waxes and resins.

Lignites in the crude state are more or less plastic and at times are greasy to the touch. They are brownish black in color, but when dry may be lighter. Pyropissite was one of the best varieties formerly used but this is no longer available; the yield of tar from this ranged from 64 to 66 per cent. Coal now considered suitable for destructive distillation gives 5 to 10 per cent of tar, 50 to 60 per cent of water, 25 to 35 per cent of coke and the rest is gas and loss. In 1905 the average yield of tar in the Thüringian district was 3.9 kilograms tar per hectoliter.* If the coke is in demand, it may be possible to distill coals yielding as little as 3 kilograms of tar

The tar is then distilled† in a vacuum or at ordinary pressure. Oily products, paraffin, red products (picene), coke and gas are obtained. The oily material is further separated into low boiling "photogen," gas-oil, naphtha, cleaning oils and other products.

According to Scheithauer the lignite tar of the Thüringian district gives 10 to 15 per cent of paraffin and 50 to 60 per cent of mineral oils. The paraffin is graded, according to its melting point, as hard or soft paraffin. The melting points lie between 35° and 60° C. The following products are obtained:

	Specific gravity at 17° C.
Solar oil	0 825 to 0 830
Cleaning oil	0 850 to 0 860
Yellow oil	0 860 to 0 870
Red oil	0 870 to 0 880
Gas oil (dark paraffin oil)	0 880 to 0 900
Heavy paraffin oil	0.900 to 0.920

* Braunkohle, **5**, 508 (1906).

† Petroleum, **9**, 160 (1913). Z. angewandte Chem., **26**, 528 (1913).

As by-products are obtained asphaltic products (lignite tar pitch and " goudron "), crude creosote, and creosote oil.*

II. Physical and Chemical Properties

(*a*) **Physical Properties.** The brown-coal lignite tar has the consistency of butter at room temperature, is yellow to dark brown in color, has a creosote-like odor (also in part like hydrogen sulphide, since this often forms in considerable quantities during the distillation). It becomes quite mobile on warming (it contains no viscous lubricating oil portions) and its solidification point lies between 15° and 30°. The tar begins to boil near 80°, though sometimes not below 100°. The main quantity passes between 250° and 350°, with some tars between 250° and 300°. The specific gravity ranges from 0.850 to 0.910.

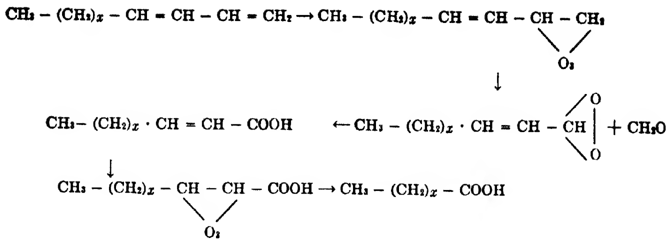
(*b*) **Chemical Composition.**† The crude tar contains, as its principal components, saturated and unsaturated hydrocarbons. The former are present in largest amount from C_7H_{16} to solid $C_{27}H_{56}$. Since brown-coal tar contains considerable amounts of unsaturated hydrocarbons, the brown-coal-tar oils (as well as the softer paraffins) have higher iodine absorption values than the corresponding oils from crude petroleum; all of these products react with concentrated nitric acid and with sulphuric acid with a much greater rise in temperature than do the oils from petroleum. There are also found small but noteworthy amounts of phenols and cresols, as well as aromatic hydrocarbons, such as benzol, and its homologues, naphthalene (0.1 to 0.2 per cent), chrysene and picene. Traces of aldehydes, ketones, pyridine bases, quinoline and sulphur derivatives are also found, but not in quantities sufficient to pay for their extraction.

By the action of ozone on lignite-tar oils (having an iodine value of from 50 to 60) Harries‡ obtained non-explosive ozonides, which, on treatment with alkali and repeated ozonizing of the unsaturated linkings, formed acidic materials, the potassium and sodium salts of which are capable of producing a lather; these materials appear to be of economic importance. The following series of reactions show the changes brought about.

* Z. angewandte Chem., **26**, 527 (1913).

† Rosenthal, Z. f. angew. Chem., **6**, 109 (1893); **14**, 665 (1901); **16**, 221 (1903); Chem. Ztg., **14**, 870. Oehler, Z. f. angew. Chem., **11**, 561 (1899). Heussler, Ber., **25**, 1665 (1892). Krafft. Ber., **21**, 2256 (1888). Ihlder, Z. f. angew. Chem., **17**, Heft 16 (1904).

‡ Chemiker Zeitung, **41**, 117 (1917).



The production of formaldehyde during the oxidation indicates the presence of an unsaturated linking adjacent to the terminal carbon; the production of other aldehydes, of ketones and simpler fatty acids indicates a complicated structure, and may mean the presence of forked-chain hydrocarbons. The product not attacked by ozone is a saturated mobile paraffin oil.

The gas produced in the destructive distillation contains 10 per cent of CO_2, 1 to 2 per cent of heavy hydrocarbons, 0.1 to 6.3 per cent of O_2, 5 to 15 per cent of CO, 10 to 30 per cent of H_2, 6.4 to 25 per cent of CH_4 (also higher homologues), 10 to 42 per cent of N_2, and 1 to 3 per cent of H_2S. Krey introduced the use of these gases in internal combustion engines and the recovery of the CO contained by producing from it salts of formic acid.

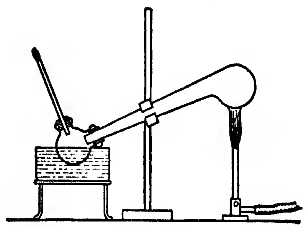


FIG. 119.

The gas-liquor* contains alcohols, aldehydes, ketones, nitriles, acetic acid and homologues, also other acids, phenols, and pyrocatechin; also some NH_3 (0.03 per cent).

The coke contains from 15 to 25 per cent of ash; it is used for fuel.

III. EXAMINATION

(a) Tar-yield on Destructive Distillation:

A weighed 200 c.c. retort (shaped as shown in Fig. 119), of hard glass, is attached to a receiver cooled with water. 20 to 50 grams of powdered coal are heated in the retort, at first with a small flame, later with a large flame, until no more vapors pass; this requires from 4 to 6 hours. The amount of coke is determined by reweighing the retort. The distillate, consisting of yellowish white, turbid water and tar, is weighed after first melting down into the receiver any tar condensed on the neck of the retort. By placing in hot water, the tar is melted and brought to the surface; after cooling, the solidified tar layer is punctured, the water poured off

* Laboratoriumsbuch, 29.

and the receiver weighed with the air-dried tar. The tar can be more accurately determined by extraction with benzol and by then evaporating the solvent. Small amounts of water are eliminated by adding small portions of absolute alcohol and then evaporating. The results thus obtained are recalculated on the basis of 55 per cent water of distillation (moisture in coal and water formed by decomposition); the theoretical yields, thus obtained, are still further recalculated commercially in that the commercial operation is supposed to give only 60 to 70 per cent of the theoretical. The tar obtained in the industrial distillation contains fewer acid components and the specific gravity is lower than is the case with the distillation products obtained by the above method.

(b) *Analysis of the Tar*

(1) **Specific Gravity.** This varies according to Graefe* from 0.850 to 0.910 (with coal tar, tar from lignite gas-producers, and wood tar it is more than 1). The specific gravity is determined, according to the methods described on page 3, with a pycknometer or hydrometer at 44°. The more valuable parts of the tar (hydrocarbon oils and paraffin) lower the specific gravity while the less valuable creosote-like materials and basic components raise the specific gravity. Very good tars have a specific gravity of from 0.820 to 0.830, the poorer sometimes higher than 0.910.

(2) **Solidification Point.** This is higher in proportion to the amount of paraffin contained. The galician method (page 246) is used.

(3) **Distillation Test.** This is most important and allows a determination of the yield of crude light oils and of paraffin.

200 grams of tar are distilled in a retort, catching the first portions, up to the point where a drop solidifies on ice, as crude light oil; the further distillate, up to the point where yellowish red, resinous masses (picene) begin to pass, is known as paraffin masses. The red portion (containing picene) is caught separately. From 1.5 to 4 per cent of coke is found in the residue. The difference in weight between the tar used and the products obtained, gives the amount of gases and loss. In exact investigations the fractions are caught at definite temperature intervals (up to 150°, to 250°, etc.), noticing also their behavior on ice.

According to Scheithauer, from a tar of the Thüringian district there was obtained 5 per cent of naphtha, 10 per cent of solar oil, 10 per cent of light-colored paraffin oil, 30 to 50 per cent of heavy paraffin oil, 10 to 15 per cent of hard paraffin, 3 to 6 per cent of soft paraffin, 3 to 5 per cent of asphaltic products, smaller amounts of creosote and 20 to 30 per cent of coke, gas and loss.

(4) **Detection of Lignite Tar.** This depends on the presence of the higher homologues of phenol; on treatment with diazobenzol chloride, the reaction described on page 202 is given.

* Graefe, Laboratoriumsbuch, 32.

(c) Examination of the Tar-Distillates

The oils (naphtha, solar oil, paraffin oil, gas oil, etc.), obtained in the distillation, rectification and pressing, are examined in much the same way as are the petroleum products. (See page 115 and following.)

The following additional points are to be considered with gas oils:

(1) **Creosote Content.** This should be as low as possible with good gas oils. For determination, see page 151.

(2) **Sulphur.** The amount can be determined with easily combustible fractions, according to Engler-Hessler (page 140) or according to Rothe (page 77). See page 302 for the sulphur content of lignite-tar oils.

(3) **Heavy Hydrocarbons.** These are soluble in concentrated sulphuric acid and are determined according to page 125. Eisenlohr determines the amount of these by repeatedly shaking 300 grams of oil with 10 per cent portions of concentrated sulphuric acid to the point where the oil no longer decreases in weight. Oil treated with sulphuric acid (according to Graefe) gives greater lighting and heating efficiency (see page 143); it also has a lower iodine value, from 9 to 15.

(4) **Distillation Test.** A gas oil is the more valuable the smaller its boiling limits; it is desirable to determine the limits within which 80 per cent of the oil distills.* The presence of creosote and of considerable amounts of unsaturated hydrocarbons, as well as components boiling over 300°, decreases the gasifying power of these oils; the quantities of these components should be determined.

The sample is distilled in an Engler flask (page 99), fifty-degree fractions being caught. In order to determine if it would pay to recover the paraffin, the amount of distillate solidifying on ice is weighed.

(5) **Content of Soft Paraffins.** The total amount of soft paraffins present† is of importance in the valuation of gas oils. According to the experiments of Eisenlohr (carried out in the apparatus of Wernecke, page 154), the higher the content of soft paraffins, the more valuable the oil for the manufacture of gas. The method of determination given by Eisenlohr requires further study however.

Besides the method described on page 108, the method of Zaloziecki (according to Scheithauer) has been found practicable. Five grams of the oil are dissolved in ten times this amount of amyl alcohol and the paraffin is precipitated with an equal amount of nearly absolute alcohol at 0°, the precipitate being filtered at this temperature.

* According to Deutsche Verbandsbeschlüsse, 1909.

† Eisenlohr, Zeit. f. angew. Chem., **10,** 300, 332 (1897); **11,** 549 (1898).

(6) **Flash Point.** This is sometimes used as a means of identification and it may be used to determine its inflammability. (See lubricating oils.) Page 38.

(7) The determination of the value of the oil for gasifying has already been considered on page 152 and following.

(8) **Color, Lighting Value and Resistance to Low Temperatures** are sometimes determined (pages 129 and following). The color has nothing to do with the ability of an oil to gasify.*

(9) **Phenol and Creosote.** Cleaning oils from lignite tar (light paraffin oils) sometimes cause trouble because the creosote-like bodies attack the hands of the laborers using them (see page 114). The oils should therefore be tested to see if they are free from such bodies (see page 151); they should not react with sodium hydroxide.

The alkaline extracts of nearly all lignite-tar distillates give the diazo-reaction described on page 201; a red color (or precipitate) will appear with lignite oils, but with petroleum products a yellow to brown color will be observed. The brown-coal tar oils are often recognized by their tarry odor.

5 c.c. of the oil are shaken thoroughly in a measuring cylinder with 30 c.c. of sodium hydroxide solution (sp. gr. 1.35) and then left 10 minutes in a boiling water bath. If a dark ring forms between the two layers, creosote is present and the presence of lignite or shale-oil products may be suspected. If the oil to be tested is too thick, it is first diluted with kerosene free from creosote.

TABLE 72

PROPERTIES OF LIGNITE-TAR OILS*

	Specific gravity ×1000	Beginning of boiling °C.	Per cent distilled at				Viscosity (Engler)	Pensky flash point °C.	Index of refraction at 17.5° C	Iodine value Hübl	Per cent sulphur
			150°	200°	250°	300°					
Naphtha	800-820	136	7	94	100	..	0 98	29	1 460	.	0 73
Solar oil ...	820-835	136	4	84	100		1 00	35	1 469	77	0 83
Cleaning oil	845-870	189	.	4	95	100	1 1	66	1 485	..... .	0 78
Yellow oil ..		204		...	68	96	1 21	82	1 490	.. ...	0 76
Red oil	875-900	207	..		34	81	1 25	85	1 497	......	0 86
Gas oil . .		201	.	....	30	78	1 4	86	1 505	63	1 36
Heavy paraffin oil	900-930	228	....	..	2	16	3 45	103	1 513	52	0 99

* Graefe, Laboratoriumsbuch, 127, 129. Petroleum, **1**, 14, 81, 632, 636 (1905).

(10) Because of their high content of heavy hydrocarbons, of phenols, and of sulphur-containing components the lignite-tar oils have on

* Deutsche Verbandsbeschlüsse, 1909.

the average a higher density than the corresponding petroleum products (Table 72).

(11) The lignite-tar oils show higher iodine values because they contain unsaturated hydrocarbons.

Iodine Values of Lignite-tar and Petroleum Products

	Hübl	Wijs
Solar oil	77.0	85.0
Gas oil	63.0	69.0
Paraffin oil	52.0	60.0
Russian kerosene	0.0	0.8
American kerosene	16.8	19.1
German kerosene	0.73	3.0
Galician kerosene	2.18	4.0
Ligroin	0.05	0.2

Sulphur Content of Lignite and Petroleum Products*

	Per cent		Per cent
Lignite-tar products:		Asphalt	1.65
Solar oil	0.83	Creosote oil	1.15
Cleaning oil	0.78	Pyridine bases (boiling up to 200°)	0.025
Yellow oil	0.76	Petroleum products:	
Red oil	0.86	Coke from Wietze petroleum	0.74
Gas oil	1.36	Coke from Pechelbronn petroleum	1.24
Paraffin oil	0.99	Gas oil from Wietze petroleum	0.35
Naphtha	0.73		
Goudron	0.97		

* Graefe, Chem. Rev., **17**, 3 (1910).

(d) Examination of Paraffin Wax

1. Paraffin content, solidification point, etc., are determined as on page 245 and following.

2. **Distinguishing between Lignitic Paraffin and Petroleum Paraffin.** Since paraffin from lignite is considered more valuable than petroleum paraffin, it is of importance to determine the source of the paraffin material.

(α) Graefe tests pure products by placing 2 c.c. of melted paraffin on the same volume of concentrated sulphuric acid and allowing to stand on a water bath, without shaking. Petroleum paraffin remains clear, or colors the acid, which however remains clear; with lignitic

paraffins, a yellow or brown color will appear and the acid will become turbid.

(β) Another difference is found, according to Graefe and Krey, in the iodine values, which for the petroleum paraffins range from 0.4 to 1.9, with the paraffins from lignite or shale from 3.3 to 5.8.

(γ) Both fail, however, with crude and partially purified products. In such a case the method of Marcusson and Meyerheim * is available; it depends on the determination of the iodine value of the oil, always present in paraffin:

100 grams of paraffin are dissolved in 300 c.c. of warm ethyl ether (it might be better to use the less inflammable chloroform) and the same volume of 96 per cent alcohol added. If much oil is present in the paraffin, 50 grams of material may be enough. The paraffin, which separates on cooling, is collected on a Buchner filter, the filtrate is freed from the solvent by distillation, the residue is dissolved in 50 c.c. of ether, and again precipitated with 50 c.c. of 96 per cent alcohol. The precipitation is brought about by cooling to − 20° (see method of Holde on page 108). The alcohol-ether solution, when separated from the precipitate, gives the oily residues on distillation of the solvent; this residue may in certain cases be still contaminated with black resinous bodies. To separate these the mass is dissolved in naphtha and filtered and the filtrate is evaporated. The iodine value of the residue is then determined (see page 409) by the Hubl-Waller method.

According to this method, the iodine value of petroleum paraffin residue is found to be 3 to 12, that of the oils from lignite or shale oil paraffin, 18 to 31. These differences are also to be found with refined products.

(*e*) *Paraffin Candles and Composition Candles*

(1) **Definition.** All paraffin candles contain small amounts of "stearine" (1 to 2 per cent), since this makes the removal from the moulds easier. Composition candles contain varying amounts of paraffin and considerable "stearine" (as a rule one-third). The candles lose their transparency through the addition of much "stearine" and approach, in appearance, the more valuable "stearine" candles; the amount of "stearine" is so regulated that the price of manufacture does not get too high, yet enough is added to cause the transparency of the paraffin to disappear. According to Krey, the amount of "stearine" in the top and bottom of a candle may differ by as much as 2 or 3 per cent; this is caused† by the unequal temperatures of the cooling water about the forms after filling the moulds.

The highest melting paraffin is not used in making composition

* Zeit. f. angew. Chem., **23**, 1057 (1910).
† Graefe, Braunkohle, **3**, 109.

candles — generally a grade melting at 50° is used; an addition of paraffin with a melting point under 49° is generally considered as an adulteration. The melting points of mixtures of paraffin and "stearine" are lower than the mean melting points calculated by the law of mixtures; the depression of the freezing point follows the law of Raoult. The melting point* of a paraffin mixture can be calculated by means of the expression $\frac{(f)(a) + (f')(b)}{a + b}$, where f and f' are the melting points of the separate components and a and b the amounts used.

(2) **Alcohol Candles.** In the past and again recently, paraffin candles to which the external appearance of white "stearine" candles has been imparted by the addition of alcohol to the paraffin, together with decidedly less "stearine" than is ordinarily found in composition candles, have been found on the market. The candles gradually become more and more transparent through the evaporation of the alcohol, and rapidly during burning.

To determine the amount of volatile additions, 5 to 10 grams of material are melted† in a weighed vessel and then a slow current of air is blown through the melted mass for 5 minutes. The difference in weight gives the amount of volatile matter.

(3) **Examination.** It can often be determined by mere inspection whether a candle is made of pure paraffin or of a mixture of materials;‡ paraffin candles are more translucent; composition candles are milky and opaque. Since the composition at the top and bottom may be different, a whole candle is melted for the analysis, the wick being removed, and samples are taken from the well-mixed melted mass.

(α) **Stearic Acid Content.** 10 grams of material are warmed with 50 c.c. of 50 per cent alcohol till melted, and then titrated with N/10 potash in the presence of phenolphthalein (KOH is better than NaOH since the potassium soaps do not solidify as easily as the sodium soaps). The titrated solution is allowed to cool, the cake of paraffin is removed, washed with water, melted with hot water and then again cooled, then dried and weighed. The wash water and the soap solution are diluted to 200 c.c. and then just acidified with hydrochloric acid; the separated stearic acid is filtered, washed free from mineral acid, melted in the presence of water, cooled and the cake, on drying, weighed. The volumetric and gravimetric values will differ only slightly.

The melting points of the separated paraffin and "stearine" acids are determined and these values will in general be found higher than the melting point of the candle itself. (Page 245.)

* Graefe, Laboratoriumsbuch, 87.

† Graefe, Laboratoriumsbuch, 110.

‡ Graefe, Seifensiederzeitung, **1909**, 1279, 1332.

The amount of oleic or iso-oleic acid (iodine number 90.1) in the "stearine" can be determined through a determination of the iodine value; an iodine value of 4.5 would correspond to a content of 5 per cent of oleic acid or of iso-oleic acid.

The paraffins can be examined as to their source (petroleum or lignite) by the method on page 303.

(β) **Soft Paraffin.** The amount of this in the paraffin separated by the previous procedure is determined according to the method on page 249.

(γ) With the photometric examination of the candles must be determined their tendency to smoke, to melt too rapidly or to develop a bad odor when extinguished. It has been shown by exact photometric examination, as described under kerosene, that pure paraffin candles, for the same amount of material consumed, give more light than do the composition candles.

(δ) **Tests for Acid Amides, Montan Wax and Carnauba Wax.** To give soft candles greater stability, the anilide of stearic acid and similar acid amides (patent of C. Liebreich), montan wax and carnauba wax are added.

The first-mentioned nitrogen compounds give the prussian blue test on melting the candle material with sodium and on treatment of the dissolved product with ferrous sulphate and ferric chloride.

The added substances can be concentrated by heating the mass 5 to 10 degrees above the apparent melting point, pressing in cloth with heated plates and treating the residue with cold benzol, in which only paraffin dissolves easily, while stearic anilide, montan wax and carnauba wax dissolve with difficulty. The latter can be identified by their saponification and acid values.* Some of Graefe's results are given in Table 73.

TABLE 73

Sample	Montan wax			Carnauba wax	
	I	II	III	I	II
Acid value	101.6	71.0	42 4	13.78	10 60
Saponification value	101.6	73 8	62 0	75 38	80 60
Ester value	....	2.8	19.6	61.60	70.00

(ϵ) **Bending Test.** This shows the tendency of the candles to bend, owing to the presence of soft paraffins.

* Graefe, Laboratoriumsbuch, 88.

Candles 22 cm. long, 16 mm. in diameter at the top and 18 mm. at the bottom are fixed horizontally in round holes bored in a board placed vertically. The free part is 21 cm. long. After standing 1 hour at 22° (Graefe advises 25°) the bend is measured in millimeters (best with a cathetometer); the greater the bend, the less valuable the candle. In examining other shapes of candles, the material must first be changed to the above form. The candle material is warmed somewhat above the solidification point, poured into the warm mould and cooled by water at room temperature. The tests should be made only with candles which have been at least 6 hours out of the moulds and at least 3 hours in the room in which the test is to be made.

Fig. 120.

Fig. 120 shows the candles after testing. No. 1 was made from lignitic paraffin of melting point 53°. No. 2 contained lignitic paraffin of melting point 50.5°. No. 3 contained petroleum paraffin of melting point 50.7°, while No. 4 was a mixture of paraffin melting at 35.3 and at 60.6°. From the figure may be seen the influence of soft paraffin on the stability of the candles, as well as the superiority of the lignitic paraffin over the petroleum paraffin. Graefe states that it has been repeatedly shown that candles made from the lignitic material are more stable than those from the petroleum paraffin of the same melting point.

B. Distillation Products of Bituminous Shale

I. Shale Tar

The obtaining of tar and oil from bituminous shale became a problem of considerable moment in Germany during the war; the industry had been unable to compete successfully with American mineral oils, but as these were cut off by the blockade, shale distillation was revived again.

Large deposits of shale are found in Scotland, Germany, Sweden, Canada, Luxemburg, and the United States. The shale on distillation yields an oil, ammoniacal liquor and gas.

The gas is a mixture of H_2 and CO, with some H_2S, O_2, N_2, CO_2 and hydrocarbons; it has considerable fuel value and is burned under the retorts, or, after de-sulphurizing, in internal combustion engines.

The oil obtained is intermediate between petroleum and lignite-tar. It has a density of 0.86 to 0.96, strong odor, dark color and contains aromatic hydrocarbons, paraffins, olefins, and naphthenes, as well as pyridine, quinoline, phenols, cresoles, mercaptans and thioketones. Heussler found in Scottish shale-tar oil (under 110°) 42 per cent of saturated hydrocarbons, 39 per cent ethylenes, and 17.3 per cent of aromatic hydrocarbons and naphthalene. A French oil contained hydrocarbons of the indene group, phenols and homologues of thiophene.

The shale oil is distilled in vertical, continuously operating retorts of Henderson, Young-Beilby, and Bryson under the action of superheated steam. In France the system of Champeaux and Penard is used.

The oil is purified much as petroleum is and after separation of acidic resinous material yields naphtha, burning oils, gas oils, lubricating oils and paraffin. The ammoniacal liquor contains free ammonia, and carbonate and sulphate of ammonia; the distillation residue is a mixture of the mineral matter in the shale and of coke.

In Scotland there was formerly distilled the so-called "torbanit" intermediate between shale and bog-head coal; it gave 408 to 490 liters of oil per ton. There is now distilled a shale from Linlithgow and Midlothian, 3,280,000 tons being converted in 1913; the deposit lies 600 to 1200 metres below the surface. It gives 140 to 170 liters per ton, though the poorer grades may yield only 67 to 80 liters of oil per ton. By dry distillation is obtained 12 per cent of oil, 4 per cent of gas and 8 per cent of ammoniacal liquor, the residue, 76 per cent, containing 9 per cent of coke. On rectification, the oil will yield 3 to 5 per cent of naphtha, 20 to 25 per cent of illuminating oil, 15 to 20 per cent of gas oil, 15 to 20 per cent of lubricating oil, 3 to 5 per cent of soft paraffin, 7 to 9 per cent of hard paraffin, and 2 to 3 per cent of secondary products (acid, basic, neutral Gudron).

In France the deposits of Buxiere and Autun are worked, a yield of from 3.75 to 4.5 per cent by volume of oil being obtained; this has a density of 0.870 to 0.910, and a paraffin content too low to be worked profitably. In 1909, 116,000 tons of shale and 6000 tons of bog-head coal were distilled. Swedish shale has a lower content of bitumen than the Scottish shales and produces about 30 to 40 liters of oil per ton of shale (in rare instances 60 to 80 liters) — the shale contains 6 to 8 per cent of sulphur.

At Messel near Darmstadt in Germany is a shale deposit 150 meters thick and about 0.75 kilometers square which lies only 4 meters below the surface. This deposit has been worked since 1885. It produces on distillation 6 to 10 per cent of oil, 40 to 50 per cent of water, and 40 to 45 per cent of residue. From 100 kilograms of shale about 30 cubic meters of gas are obtained. The oil, of density 0.855 to 0.860, is a greenish brown material of buttery consistency; on rectification, naphtha, gas oil, motor oil, cleaning oil, lubricating oil, and paraffin are obtained, also ammonium sulphate from the ammoniacal water.

In Württemberg is found a deposit containing 12 per cent of bitumen; it yields 10 per cent oil, 2.5 per cent of gas according to Engler, and 4 to 6.5 per cent of oil and 3.7 to 5.2 per cent of gas according to other investigators. Luxemburg also has a similar shale yielding 2.3 to 5.1 per cent of oil, 5.6 to 12.1 per cent of "ammoniacal liquor," up to 5.5 per cent of gas, and 4 to 5 per cent of carbonaceous material. The oil is liquid, has a density of 0.955 and gives burning and lubricating oils on rectification.

The shale products are examined by the methods described under lignite-tar oils.

II. Ichthyol

(*a*) **Definition.** By the term ichthyol is understood in general a water-soluble oil which is obtained by the distillation of bituminous shales (from Seefeld, Tyrol) and subsequent sulphonation and neutralization with ammonia or soda; it comes on the market under the name ammonium sulfoichthyolicum, etc., and up to 1900 was exclusively prepared by the Hamburg firm of Cordes, Hermanni & Co.* In the last few years, several substitutes have entered into competition with this under the names of ichthyopon, etc. The ichthyol is used for its supposed therapeutic value in the case of rheumatism, eczema, inflammations, etc.

By the distillation of small pieces† of bituminous rock in a vacuum, and with the application of superheated steam, a thick brown oil with a faint odor, containing sulphur, of specific gravity 1.0 and viscosity 17.7 is obtained; this is easily sulphonated and is supposed to have greater therapeutic value.

(*b*) **Properties of the Crude Oil.** The oil used to prepare ichthyol is transparent, brownish yellow, of specific gravity 0.865 and boiling

* Lüdy, Chem. Ztg., **27**, 984 (1903).

† N. Zwingauer, D. R. P. 216,906; Chem. Ztg. Rep., **34**, 26 (1910).

limits 100° and 255°. The different fractions have the odor of mercaptans and yet a petroleum odor. Small amounts of nitrogenous bases are separated by the action of dilute acids; they have the odor of Dippel's oil. The vapors color concentrated sulphuric acid, violet to blue.

Elementary analyses gave the amount of carbon as ranging from 77.25 to 77.94; hydrogen 10.5 per cent, sulphur 10.7 and nitrogen 1.1 per cent.* According to Schroeter† the crude oil contains 2.5 per cent of sulphur. This becomes 10 per cent through sulphonation. It appears, therefore, that Baumann and Schotten (on whose tests the following rests) had under examination a product entirely different from that tested by Schroeter.

Scheibler‡ found in bituminous tar-oils, rich in sulphur, inden-like hydrocarbons, phenols, thiophene derivatives (propylthiophen).

(*c*) **Properties of Ichthyol.** It is soluble in water with a brown color and with fluorescence. Stronger acids precipitate from the solution a resin which is a nitrogen-free organic acid, soluble in water, from which solution it is again precipitated by mineral acids. (Noteworthy is the similarity between turkey-red oil and ichthyol, see page 480.) Ichthyol is free from nitrogen according to Baumann and Schotten; these authors tested only the sodium salt as they gave the formula $C_{28}H_{36}Na_2S_3O_6$ to the product which they examined. They found 15.73 per cent of sulphur; it appeared to be present in part as a sulpho-group and in part as mercaptan sulphur or as a thio-ether with sulphur directly united with carbon. Since the sulphonic acids as such have no action on the animal organism, the therapeutic value is probably due to that part of the sulphur directly united to carbon, while the sulpho-group only determines the easy solubility in water and consequent easy absorption.

(*d*) **Testing.** According to the committee of the German Pharmacologists of 1886, ichthyol should be easily soluble in water or in a mixture of equal parts of ethyl alcohol and ether. According to Lüdy (see above) it may contain ammonium sulphate and traces of oil.

* Baumann and Schotten, Pharm. Zentralh., **1883,** 447.

† Ibid., **1883,** 113.

‡ Ber., **48,** 1815 (1915).

C. Peat Tar

I. General

The wide distribution of peat in bogs has been the cause of many patents hoping to utilize* these deposits. The economical removal of the contained moisture (independent of the weather) is one of the greatest problems connected with this question; the moisture may make up 90 per cent of the total. One of the most advantageous methods is to distill the peat destructively, using the products of combustion to preheat the material. The peat coming from the presses, after drying, may be transported unchanged or may be left in piles exposed to the air. Most of the patents up to a few years ago were too complicated and did not cause a sufficient decrease in the volume of the peat. A gasification in gas producers is recommended.†

In the distillation, the peat is either entirely coked (the coke is used in metallurgy) or half-coked, the product being then a good fuel. The products of distillation are 2 to 4 per cent of tar, 36 to 40 per cent of aqueous distillate and 12 to 21 per cent of gases.

The peat tar resembles lignite tar and is refined into small amounts of photogen, solar oil, gas oil, paraffin and the accompanying creosote. It is as yet a relatively unimportant industry.

According to Höring peat-tar contains phenols‡, cresols, guaiacol, pyrocatechin, fatty acids (valerianic acid and homologues, which are separated from phenols by their solubility in aqueous soda solution), pyridine bases, and saturated and unsaturated hydrocarbons. Phenols and paraffin, but not pyridine, it is said, can be economically recovered from peat-tar under German conditions. But it is doubtful if the recovery of hydrocarbons can be done profitably as it is difficult to separate the creosote.

II. Analysis

(*a*) **To Distill Experimentally in the Laboratory,** an average sample of 5 kilograms is heated in an iron retort. The ash content should not be greater than 8 per cent. Seventy per cent of the tar obtained is taken as the yield in the industry. The peat to be distilled still contains 20 to 30 per cent of water.

* A. Hansding, Handbuch der Torfgewinnung und Torfverwertung, Berlin, 1917. P. Höring, Moornutzung und Torfverwertung, Berlin, 1915.

† Z. angewandte Chemie, **21,** 1597 (1908). Also D. R. P. 158,032, 176,364 and 176,365.

‡ Börnstein and Bernstein, Die Phenole des Torfteers, Z. angewandte Chem., **27,** 71 (1914).

Corresponding to the position of peat intermediate between wood and coal, the aqueous distillate will contain ammonia, methyl alcohol and acetic acid.

(*b*) **Analysis of the Aqueous Distillate.** Ammonia is determined by distillation with sodium hydroxide and collecting the ammonia in N/2 sulphuric acid; it is calculated as ammonium sulphate (1 c.c. of N/2 acid is equivalent to 0.033 gram of ammonium sulphate). After separating the ammonia, the acetic acid is determined by distilling with steam, after acidification with phosphoric acid, and is then titrated with N/1 sodium hydroxide (1 c.c. of sodium hydroxide is equivalent to 0.079 gram of calcium acetate). The methyl alcohol is determined, after repeated rectification in a column apparatus and treatment with red phosphorus and iodine, as methyl iodide. This distills and is caught under water and its volume determined in a graduated cylinder. If 5 c.c. of alcohol are used, the number of cubic centimeters of methyl iodide multiplied by 12.48 gives the volume per cent of methyl alcohol.*

(*c*) The tar is analyzed as described under lignite tar. No definite specifications can be set.

The chemical composition of crude shale oil and of the products of the destructive distillation of peat is very similar to that of lignite tar qualitatively; the quantitative relations are not the same. From peat tar are obtained on the average 10 to 20 per cent of turf or solar oil, 10 to 20 of middle oil, 1 to 4 per cent of paraffin, 30 to 40 of creosote, and 20 to 30 per cent of coke and loss.

D. Wood Tar†

I. General

Wood contains cellulose ($(C_6H_{10}O_5)x$), lignin ($C_{19}H_{24}O_{10}$), water, dextrin, starch, sugar, proteins, resins, essential oils, tannic acid, colored substances, and mineral matter. On distillation there are obtained charcoal, water, and volatile organic substances, acetic acid, methyl alcohol and acetone. At 400°, which is the maximum temperature at which tar may be produced, charcoal, water, carbon monoxide and dioxide, tar, aqueous acetic acid, and various gases are obtained. The gases may be burned as fuel or in internal combustion engines.

The tar is partly dissolved, and partly suspended, in the acetic acid. In distilling coniferous wood (which contains rosin, that is, abietic acid) terpene hydrocarbons are produced; these float on the acetic acid. If the tar products are allowed to settle slowly there is

* Klar, Holzverkohlung, **1904**, 223.

† With the assistance of J. Budowski.

obtained a tar which is different from that left in the still after driving off the solvent.*

TABLE 74

Kind of tar	Solubility in					Characteristic Reactions
	Acetic acid 95 per cent	French turpentine	Chloroform	Absolute ether	Anilin	
Pine tar	Complete	Soluble	Soluble	Soluble	Soluble	Petroleum ether extract of the tar gives a green color with copper acetate solution (1 to 1000).
Beech tar	Complete	Little soluble	Part insoluble	Part insoluble	...	Petroleum ether extract of the tar gives no color with copper acetate solution (1 to 1000).
Juniper tar	Not complete	Soluble	...	... ...	Soluble	An aqueous extract (1 to 20) gives a red color with ferric chloride solution (1 to 1000).
Birch tar	Not complete	Soluble	. ...	......	Part insoluble	An aqueous extract (1 to 20) gives a green color with ferric chloride solution (1 to 1000).
Aspen tar	Not complete	Part insoluble	Part insoluble	Part insoluble	......	

A tar obtained on destructively distilling the wood of deciduous trees yielded acetic acid (about 2 per cent), wood alcohol (0.6 per cent), water (18 per cent), light oils (of 5 per cent density 0.97), heavy oils (of 10 per cent density 1.043), wood-tar pitch (62 per cent), and gases (2.4 per cent). A tar from conifer wood gave pyroligneous acid 12 per cent,

* Stahl u. Eisen, 733, 771 (1907). Klar, Technologie der Holzverkohlung; 57.

terpenes about 30 per cent, and tar about 58 per cent. If the solvent material is driven from a tar, the residual tar contains aldehydic and phenolic bodies.

II. Properties of the Tars

(*a*) **Tar from Coniferous Trees.** This contains pine-oil terpenes and acidic components of the resin (abietic acid) carried over by the vapors during distillation. The aqueous extract of the tar is yellow and reacts acid (coal-tar gives an alkaline reaction because of the ammonia it contains). The tar can be melted up with fat, for example, lard, (beech-wood tar cannot). The genuine tar has a sticky consistency like rosin; it is light colored and does not darken on drying. Good tar should float on pyroligneous acid, because it contains turpentine oil and light rosin oil which have a low density.

(*b*) **Beech Wood Tar** is a brownish-black, oily liquid, denser than water, of sharp, empyreumatic, creosote-like odor. The aqueous extract reacts acid (acetic acid) and acquires the odor of the tar. It contains polybasic phenols (guaicol and pyrogallol) (conifer tar does not).

(*c*) **Birch Tar** (obtained from Poland and the Russian province of Minsk) is a thin, yellow green liquid with an odor of Russia leather. It has a density of 0.926 to 0.945 at 20°. It is often adulterated with pine tar. Pine tar is completely soluble in 96 per cent alcohol, in 96 per cent acetic acid or in anilin (birch tar does not dissolve). Birch tar is used in the preparation of Russia leather; it also is added to liquor as an aromatic.

E. Turpentine Oil and Substitutes

I. Turpentine

Turpentine oil* is the most important solvent and diluent of varnishes and paints. It is obtained on distilling the crude oleo-resin (balsam) of pine trees with steam or in a vacuum; the varieties are of American, French and Greek origin. The Greek oil (from pinus halepensis) contains dextro-pinene. The American and French oils also contain pinene ($C_{10}H_{16}$); the French (also Spanish and Portugese oils) oil contains the laevo-pinene (from pinus maritima), the American oils are generally dextro-rotatory, though sometimes laevo-rotatory oils are found, depending on the species of pine used.

* Gildemeister-Hoffmann, **2**, 12. Schimmel & Co., Apr., **1912**, page 122, Chem. Umschau., **20**, 60 (1913).

The earlier assumption that turpentine oil (which easily absorbs oxygen) contains ozone is incorrect; the presence of hydrogen peroxide and organic peroxides has been demonstrated.*

The latter (as camphor peroxide) react with water to form acidic material and hydrogen peroxide. Oxidized turpentine liberates iodine from potassium iodide; H_2O_2 does not do this alone.†

Greek turpentine (as well as the oleo-resin) is used to clarify Greek wine; the oil skimmed off is then often colored yellow, but the color can be removed by distillation.

II. Substitutes

As substitutes‡ for turpentine may be used the high-boiling naphtha already described (page 128), high-boiling benzene hydrocarbons such as solvent naphtha and heavy benzol, chlorinated hydrocarbons (tetrachloride of carbon, and trichlorethylene), as well as the distillation products of rosin (colophony) namely rosin spirits, "wood spirits of turpentine," pine oils, and camphor-oil fractions.

Pine oil§ is obtained on distilling the stumps and roots of pine trees. The German source of supply is Eastern Germany, Poland, Finland and Sweden. The pine oil contains dextro-pinene and dipentene, limonene, cymene and other terpenes, boiling at from 170 to 180°.

"Wood spirits of turpentine"‖ are obtained by the distillation or carbonization of resinous wood and rectification of the tar, or by extraction with hot rosin from which the oil is separated by superheated steam. It contains pinene, dipentene, camphene, limonene, terpineol and other bodies. By direct distillation of the wood with superheated steam is obtained a product which on rectification yields a turpentine substitute. It has a sharper, more disagreeable odor than pure turpentine oil and absorbs less iodine than turpentine. Color reactions are of no value¶ in distinguishing these materials.

Terpenes are obtained in the production of wood-pulp by the sul-

* Kingzett, J. Chem. Soc., **27**, 511 (1874).

† Berichte, **31**, 3046 (1898).

‡ Milleilungen, **26**, 157 (1908). Chem. Zeitung, **33**, 966, 978, 985 (1909); **34**, 285 (1910); **36**, 413 (1912). Herzfeld, Z. öff. Chem., **9**, 454 (1903). Berichte, Schimmel & Co., 1911 to 1917.

§ Z. angewandte Chemie, **29**, I, 361 (1919).

‖ Veitch and Donk, U. S. Dept. of Agriculture., Bureau of Chem. Bulletin, No. 144 (1911). French and Withrow, J. Ind. Eng. Chem., **6**, 248 (1914). Adams and Hilton, J. Ind. Eng. Chem., **6**, 378 (1914); **7**, 957 (1915). Whitaker and Bates, J. Ind. Eng. Chem., **6**, 289 (1914).

¶ Parry, Chemist and Druggist, **1912**, 340; Chem. Zentrallblatt, **2**, 1157 (1912).

phate and sulphite processes. In using resinous (coniferous) wood in the sulphate process, there is formed from the resins of the wood an oil volatile with steam; about 1 to 1.5 kilograms of oil is obtained from the digestion* of one ton of spruce pulp, about 10 kilograms from pine wood, but since it contains mercaptans and other sulphur derivatives (methyl sulphide) it has a very disagreeable odor. On purification, it yields a product very similar to turpentine; density 0.866 to 0.864; $[\alpha]_{D20}$ ranges from + 17.05 to + 18.55°; n_{20} from 1.4715 to 1.4727; boiling point from 154 to 155° and 167 to 168°. It consists principally of d-α-pinene, and some β-pinene. Eighty per cent of cymene (it is oxidized to iso-propylbenzoic acid and terephthalic acid) is said to be present; a terpene of boiling point 136 to 138° at 9 mm, a diterpene, and a solid body of melting point 67° insoluble in alcohol have also been described.

Camphor oil is obtained as a by-product in the production of Japanese camphor from the camphor tree (Cinnamomum Camphora). It is substituted for turpentine because of its solvent powers and has been imported into Europe since 1887. After the Japanese took possession of Formosa they perfected the recovery† of camphor and camphor oil. Chips of wood from trees (at least 50 years old), as well as roots, branches, and leaves, are subjected to steam distillation; the oil collected on the surface of the water in the receivers contains camphor crystals which are filtered off, and pressed. Such oil when brought into the European market was formerly treated (by fractionation and crystallization) to remove dissolved camphor and safrol;‡ these materials are now however removed in Japan.

Three grades of camphor oil are found on the market: light, heavy, and blue oil.

1. Light camphor oil is colorless with the odor of camphor; this represents the most important fraction. It contains pinene, camphene, dipentene, limonene, phellandrene, all of the composition, $C_{10}H_{16}$, also cineol $C_{10}H_{16}O$ (of boiling point 176°). If the price is right it is used as a diluent of turpentine; it is also used for the solution of resins and lacquers, for the perfuming of cheap soft soap (2 to 3 per cent addition), and for cleaning type, etc. It has a specific gravity ranging from 0.860 to 0.910, a boiling point between 175 and 200°, and a solidification temperature of from 45 to 60°.

* Holse and Dedichen, Berichte, **50,** 623 (1917). Also **33,** 2343 (1900). Chem. Zeitung, **40,** 945 (1916).

† Davidson, "The Island of Formosa," **1903.** 397 to 443. Adolf Fischer, Streifzüge durch Formosa, **1900.**

‡ Schimmel & Co., Oct. 16, **1902** and Sept. 7, **1885.**

TABLE 75

Turpentine and Substitutes

		Specific gravity at 15° × 1000	Boiling limits	Refractive index n at 15°	Optical rotatory power	B = bromine value I = iodine value
Turpentine (fresh)		862 to 889	75 to 80 per cent distills between 155 and 165°, the rest under 175°	1 471 to 474	French −29 to 34.8° American* + 9 to +14° Greek + 30°	B greater than 1.9 generally 2 15 to 2.3** I from 350 to 400
Regenerated turpentine***		856 to 874	Boiling begins between 164 and 176°, 0 to 10 per cent distills under 165°, 75 to 100 per cent, under 175°	1 476 to 1 479	+0 08 to 6 7°	B from 1.6 to 1.9
Pine oil		865 to 874	170 to 180°		+14 to 24°	B from 1.6 to 1.9
Wood spirits of turpentine	Dry distillation	859 to 915	Boiling begins between 153 and 177°, 0 to 95 per cent distills under 170°; 20 to 98 per cent, under 185°	1 467 to 1 476 at 20°	+16.5 to 36.1°	I from 300 to 362
	Steam distillation	857 to 898	Boiling begins between 150 and 166°; 0 to 93 per cent distills under 170°, 61 to 97 per cent, under 185°	1 467 to 1.481 at 20°	+34 4 to 77.6°	I from 300 to 398
Rosin spirits			under 150°			. .
Naphtha Boiling point 100 to 180°	American	734	100 to 180°	1 419 to 1.450	practically 0	very small
	Russian	770 to 789	same	same	same	same
	Galician	760 to 766	same	same	same	same
	Indian	781 to 803	same	same	same	same
High boiling naphtha		820	160 to 200°	same	0	0
Benzol		885	80°	1 502	0	0
Toluol		870	111°	1 489	0	0
Xylol		868	133°	1 496	0	0

* Indian turpentine (from Pinus excelsa) has $[\alpha]_D = +42°\ 30'$. The oils of Pinus Khasya show $[\alpha]_D = -0\ 76°$, of Pinus longifolia $[\alpha]_D = 5°\ 30'$; these are less valuable.

** Old resinified oils are rectified, the new distillates being then examined; in genuine samples, the correct bromine value is given.

*** Obtained as a by-product in the manufacture of camphor from American turpentine oil. It contains pinene and limonene, also terpineol and cymol; these boil near 175°. See Semmler, Die Aetherischen Oele, **1906, 3,** 359.

TABLE 75

TURPENTINE AND SUBSTITUTES. *Continued*

		Specific gravity at 15° × 1000	Boiling limits	Refractive index n at 15°	Optical rotatory power	B = bromine value I = iodine value
Solvent naphtha		869 to 882	125 to 200°	1 498 to 1 501	0	0
Heavy benzol		920 to 945		1 525	0	0
Carbon tetrachloride		1599	77 to 78°	.	0	0
Trichlorethylene		1470	88°	.	0	0

2. Heavy camphor oil contains the sequi-terpenes $C_{15}H_{24}$ bisabolene and cadinene; the latter gives, when dissolved in glacial acetic acid, on treatment with one drop of concentrated sulphuric acid, a beautiful color test (green to blue, then red*). Safrol $C_{10}H_{10}O_2$, eugenol $C_{10}H_{12}O_2$, fenchone $C_{10}H_{16}O$, and terpeneol $C_{10}H_{18}O$ are also present. The specific gravity is 0.950 and the boiling limits, 270 and 300°.

The oil is used for same purposes as the light oil, and for covering the odor of shoe blacking, mineral oils, and wagon greases.

3. Blue camphor oil is used for the same purposes as the heavy oil and has a specific gravity ranging from 0.950 to 0.960.

III. ANALYSIS

The following properties, described under (*a*) and (*b*), are those of fresh oil.

(*a*) *Physical Tests*

1. **Specific Gravity.** See Table 75.

The coefficient of expansion of turpentine equals 0.001; the change of the specific gravity for 1 degree change in temperature is 0.00085.

2. Boiling limits are given in Table 75.

3. **Refractive Index,** see Table 75.

Large additions of benzol-hydrocarbons are recognized by the refractive index of the mixture, small amounts added are detected by the refractive index of the distillates. Change in refractive power per degree at 15° is 0.00035.

* Wallach, Lieb Annalen, 238, 87 (1887).

4. **Optical Rotatory Power,** Table 75.

(b) Chemical Tests

5. **Bromine Value.** See Table 75.

Turpentine and pine oils contain a double bond and a carbon bridge and therefore absorb two molecules of bromine; naphtha, benzol derivatives, and chlorinated hydrocarbons absorb only small amounts or none. The bromine value is the number of grams of bromine absorbed by 1 c.c. of turpentine at 20° C.

0.5 gram of turpentine is mixed with 50 c.c. of absolute alcohol and 5 c.c. of 25 per cent hydrochloric acid; to this solution is added from a burette some of a solution of 13.926 dry potassium bromate and 49.633 grams of potassium bromide in 1 liter of water until the liberated bromine is no longer absorbed by the turpentine and the latter remains at least 1 minute faintly yellow in color. With pine oils, however, the yellow color cannot be used as a guide since the bromine continues to be absorbed even after the yellow color appears; in this case a portion tested with zinc iodide-starch solution will show an excess of bromine.

Since 40 milligrams of bromine are liberated by 1 c.c. of the solution, the amount absorbed can be easily calculated. The bromine value is also very much lower in the case of resinified turpentine oils, but if such oils are rectified the distillate will show the normal bromine value. * According to the generally accepted results of Schneider and Zetsche, 0.5 c.c. of turpentine oil require at least 25 c.c. of the described bromine solution. If less than 25 c.c. of the solution are used the turpentine was probably adulterated.

To determine the presence of turpentine in mineral oil, the bromine absorption test is used; this is done qualitatively very easily by allowing bromine vapor to act on the oil, or by shaking the oil with bromine water and observing if the color disappears. (See page 126.) The optical rotatory power, the odor and the formation of pinene nitroso-chloride on treatment with amyl nitrite and concentrated hydrochloric acid are also useful. The latter test is carried out as follows: 1.5 c.c. of 33 per cent hydrochloric acid is dropped into a cooled mixture of 5 grams of the oil to be tested, 5 grams of glacial acetic acid and 5 grams of amyl nitrite. The separated crystals are purified by solution in chloroform and precipitation with methyl alcohol. Melting point 102 to 103°; if the crystals are allowed to react with benzylamine, in the presence of alcohol, a characteristic compound, melting at 122 to 123°, is obtained.

6. **Solubility in Alcohol.** Pure turpentine oils dissolve in 5 to 12 parts of 90 per cent alcohol; mineral oil distillates are almost insoluble in this.

7. **Solubility in Fuming Nitric Acid.** Pure turpentine oils are completely soluble at −10°, in acid of specific gravity 1.52. Petroleum naphthas are soluble only in so far as they contain aromatic and olefin hydrocarbons. Naphthas dissolved by the nitric acid are mainly aromatic in nature.

* Chem. Ztg., **23**, 686 (1899).

The test for naphtha additions is made by the method of Burton as modified by Rothe and later by Marcusson and Winterfield.* The apparatus used† is shown in Fig. 121. The method of analysis is as follows:

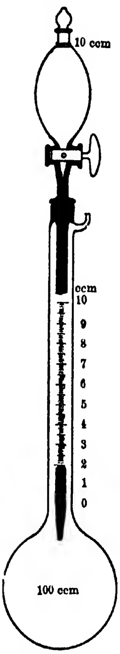


FIG. 121.

The flask contains 30 c.c. of fuming nitric acid (1.52) cooled to − 10° by a salt-ice freezing mixture. The separatory funnel above is filled up to the 10 c.c. mark with turpentine; the latter is run, drop by drop, with continuous shaking, into the cooled acid in the course of not less than 45 minutes; the higher the amount of naphtha contained the more rapidly this may be done. The mixture is allowed to stand 15 minutes after completion of the reaction and then enough concentrated (not fuming) nitric acid (at − 10°) added to the contents of the flask until the oil on the surface is brought into the graduated neck. The volume is read when the neck is at room temperature, the body of the flask being still in the freezing mixture.

The mixture is transferred to a separatory funnel, the lower layer run off into a 500 c.c. measuring flask containing 150 c.c. of water. The neck should be graduated for a 10 c.c. portion into tenths. The temperature will rise and according to the amount of naphtha present, more or less oil will separate. The unattacked oily layer in the separatory funnel is washed with water and then examined for index of refraction, specific gravity and boiling point. The aqueous layer of the nitric acid is warmed for 15 minutes under a hood to dissolve as completely as possible the resinous substances formed from the turpentine. If oil drops float in or on the liquid, naphtha-hydrocarbons may be suspected; the tests given on page 321 are then made. The cooled liquid is then shaken with 100 c.c. ether, the aqueous layer separated and the ether layer again washed free from acid with water, then with potassium hydroxide (50 grams KOH in 500 c.c. water and 50 c.c alcohol) and again with water. The ether solution dried with calcium chloride is filtered, the solvent evaporated and the residue weighed after short heating on a water bath. The residue consists of a reddish brown oil (aromatic nitro-derivatives) and is to be recalculated to c.c. since the naphtha determination was started volumetrically. The error is about 2.5 per cent.

Table 76 gives the specific gravities of the portions insoluble in the nitric acid.

From the specific gravity of the part insoluble in acid, some conclusions may be drawn as to the source of the naphtha. If the amounts of naphtha are very small, the above method will not be accurate for the small amounts will be more attacked; in this case the specific gravity of the unattacked portions will be lower.

* Chem. Ztg., **1909**, 987.

† Vereinigte Fabriken für Laboratoriumsbedarf, Berlin, N.

TABLE 76

Origin of the Naphtha Boiling limits 100 to 180°	Specific gravity	Portions soluble in nitric acid per cent	Specific gravity of the portion insoluble in nitric acid
Sumatra	0.782	22	0.76 to 0.77
Sumatra	0.803	40	
America	0.734	10	0.72 to 0.73
Russia	0.789	10	0.78
Russia	0.790	8	
Galicia	0.760	17	0.74 to 0.75

8. **Benzol Hydrocarbons.** These can be detected by the nitric acid* test. The aqueous solution of the components soluble in fuming nitric acid, obtained according to page 320, after boiling 15 minutes on a water bath, is allowed to cool for several hours. If only very little resinous material is to be seen (generally floating near the surface, benzol hydrocarbons need not be suspected). If, however, red brown drops of nitro-derivatives separate, they are forced into the graduated part of the measuring flask by adding (1.6 specific gravity) sulphuric acid, the volume read off being taken as a measure of the amount of benzol-hydrocarbons in the sample. If the separated material is over 50 per cent, the boiling will be unnecessary, and the amount is found by dividing the observed volume by 1.15.

9. **Carbon Tetrachloride and Trichlorethylene.** See Table 75. The halogen test with copper in a bunsen flame is made; an intense green color results. By boiling with alcoholic potash, potassium chloride is precipitated. A quantitative determination is made by determining the halogen by the Carius method, carbon tetrachloride containing 92.2 per cent of chlorine.

10. **Detection of Pine† Oil.** See page 266. On treatment with acetic anhydride and a drop of concentrated sulphuric acid, it gives a strong color reaction (brown red to blue violet); while pure turpentine gives a faint yellow to red coloration. The color due to the pine oil is strongest in the sylvestrene fraction (boiling point about 175°). In mixtures with turpentine, pine oil is detected by its unpleasant odor, by the sylvestrene reaction and its behavior on distillation.

(*a*) H. Herzfeld states that if the amount of pine oil is not too small, a piece of potassium hydroxide will be covered with a yellow brown film very quickly, while pure turpentine requires a much longer time to develop this color. Older, resinified turpentine oils will also form this brown layer quickly, though by distillation the resinous material may be kept back and the pine oil detected in the distillate.‡

* Marcusson, Chem. Ztg., **36**, 413 (1912).
† Chemical Abstracts, **6**, 1373 (1912).
‡ Z. öff. Chem., **9**, 456 (1903).

Pine oil, but not turpentine or refined pine oil (for example, by the Kaas method), is said by Herzfeld to give a yellow green color with sulphurous acid.

(β) A test given by both crude and refined pine oil, depending on reduction, allowing the detection of 5 per cent of pine oil in turpentine (old oils are to be first distilled and the distillate tested), has been described by Wolff.*

5 c.c. of the sample are boiled with 5 drops of nitrobenzol; then 2 c.c. of 25 per cent hydrochloric acid are added and the mixture heated 10 seconds to boiling (Danger! pine oils react vigorously). Both crude and refined pine oils, give a brown coloration in the oily layer and a brown to black color in the acid; turpentine oils give no color or only a pale yellowish green, the acid taking on a dirty green color.

(γ) Utz † states that all pine oils, even mixtures with turpentines, when treated with official stannous chloride solution (Bettendorf's reagent) develop a raspberry red color in the stannous chloride solution or in the oil, while turpentine gives only a yellow or orange-yellow color.

(δ) To detect 10 per cent of pine oil in turpentine oil, Piest ‡ suggests the following: 5 c.c. of the oil are shaken with 5 c.c. of acetic anhydride, 10 drops of concentrated hydrochloric acid added and then after cooling with water, 5 drops more are added. Allowed to stand at room temperature, a color will develop. A clear solution will form; turpentine remains water-white, pine oil becomes black. 5 per cent of pine oil will still give a dark color. Old turpentines should previously be distilled.

The methods of Wolff, of Utz and of Piest have been found useful by the Materialprüfungsamt.

11. **Rosin Spirits.** This material (boiling under 150°) is used as a substitute, being detected by its volatility. In many cases a lowering of the bromine absorption value as well as the behavior on distillation indicates an adulteration.

TABLE 77

Origin of sample	Specific gravity	Fraction I up to 150°, c.c.	Fraction II 150° to 180°, c.c.	over 180°, c.c.	Utilizable portion
Dry pine	0.924	40	82	28	69
Dry pine	0.930	48	69	33	58
Dry distillation process	0.913	6	91	45	86
Dry distillation process	0 913	9	110	34	105
Crude product from sulphate process	0.873	1	134	18	134
Another sample from sulphate process	0.873	3	134	13	134

* Farbenzeitung, **17**, 21 (1912).

† Chem. Rev., **12**, 100 (1905).

‡ Chem. Ztg., **36**, 198 (1912). See also Chem. Abstracts, **6**, 1373 (1912).

Zune distills about three-fourths of the sample and determines the refractive index of the first quarter and of the residue; with pure turpentine the difference is said to be no greater than 0.004, but with rosin oils it is decidedly greater; in the presence of 1 per cent of rosin oil it is said to change 0.006. Grimaldi[*] states that rosin spirits on heating with an equal volume of conc. hydrochloric acid and a bit of tin give a green color on cooling, by which 5 per cent can be detected in turpentine and 10 per cent in mixtures with pine oil.

12. For estimating[†] the value of the terpenes obtained from wood by the sulphate process 150 c.c. are distilled from a short-necked flask with dephlegmator so rapidly that 3 to 4 c.c. pass in one minute. The fraction from 150 to 180° is shaken with 10 per cent caustic soda solution; the insoluble residue of this fraction represents the utilizable portion. Results obtained by this method are shown in Table 77.

TABLE 78

RAILWAY SPECIFICATIONS FOR TURPENTINE IN FORCE BEGINNING OF 1913

State	External appearance	Specific gravity 15°	Distillation	Other properties
Prussia, 1901	Clear and colorless	0 860–0 880 at 20°	....	Free from admixture and completely purified. When volatilized, American or French oil should leave not more than 0 3 resinous material; Polish or German not more than 0 6.
Bavaria, 1900	Water-white, with a mild, aromatic odor	0 860–0 890	Non-volatile residue less than 1 per cent	Best refined, no additions of rosin, hydrocarbons, etc.
Saxony*	Clear, water-white, to faint yellow color	0 860–0 880 at 20°	Between 150° and 165° at least 75 per cent should distill, 25 per cent between 165° and 185°	Pure, free from fatty components and similar substances,† giving not more than 2 5 per cent residue by evaporation at room temperature.
Württemberg, 1904	Water-white with mild odor	0 860–0 890	Completely volatile, boiling limits 150–170°; no noticeable resinous residue	Used for varnishing, should contain no resins or foreign hydrocarbons. A drop on paper should leave no rings on evaporation. Shaken with an equal volume of ammonia, the two layers must appear clear and colorless
Baden, 1910				
Imperial Territory, 1912	Mobile and colorless	0 86		Rectified, must volatilize without residue and must be well adapted for thinning paints.

* Turpentine substitute, clear and colorless, mild odor, neutral; specific gravity at 15° not below 0.78; 99 per cent distilling between 120° and 180°, flash point over 21°; only traces of material, non-volatile at room temperature; should not evaporate more quickly than turpentine.

† Free from distillates from petroleum, coal tar, lignite tar, rosin or pine.

* Chem. Ztg., **31**, 1145 (1907).

† Klinga, Chem. Umschau, **24**, 91 (1917).

SPECIFICATIONS OF THE ROYAL POWDER MILLS OF SPANDAU FOR TURPENTINE OIL AND FOR PINE OIL (1911)

Turpentine for Varnish. This is to be used in preparing copal and asphalt varnish and must be commercially pure, colorless, or of a faint yellow color, clear, of characteristic odor and free from rosin oils, fats, mineral oils and naphtha.

Residue on rapid evaporation should be not more than 0.5 per cent. Bromine absorption for 1 c.c. not less than 2.0. Boiling limits 155 to 165°, at least 90 per cent passing between 155° and 165°. Specific gravity at 15°, 0.860 to 0.870

For Paints. This turpentine should be colorless to pale yellow, clear, mobile, volatile, having a strong resinous but not burnt or rancid odor, insoluble in water, barely soluble in dilute alcohol, but miscible in all proportions with absolute alcohol, ether, benzol, chloroform, fats and volatile oils. Residue on rapid evaporation less than 0.5 per cent. Boiling limits 150 to 180°. Specific gravity at 15°, 0.855 to 0.890. Applied with a pigment, it should dry well and give a hard and not sticky surface.

Pine Oil (German). It must be refined, clear and should have at the most a pale yellow color. Should form no deposit and must be free from mineral acid and impurities like hydrocarbons. Should not have a strong burnt odor, not more acidity than is equivalent to 2.12 oleic acid. Residue on distillation of pine oil for paints and varnishes should be less than 0.5 per cent, for other purposes 3 per cent is permissible. This is to be determined by rapid distillation.

F. Coal Tar and Coal-Tar Products

I. Composition of Crude Tars

Coal tar* is obtained as a by-product in the manufacture of coke (coke-oven tar) and in the manufacture of illuminating gas (gas-tar); of lesser importance are oil-gas tar, water-gas tar and blast-furnace tar. The yield of tar in the manufacture of illuminating gas from coal is about 4.7 per cent of the coal; in the manufacture of coke the yield ranges from 2 to 6 per cent, according to the coal and the construction of the retorts. Its color is due mainly to suspended carbon particles and to dark-colored hydrocarbons of high molecular weight. The specific gravity varies with coal tar from 1.1 to 1.28, with other tars† from 0.954 to 1.22. As a rule the specific gravity of coal tars is over 1, blast-furnace tar and oil-gas tar (according to the manner of gasification) may have a specific gravity under 1.

In the main the coal tars consist of aromatic hydrocarbons, phenols, pyridine derivatives, and members of the thiophene series.

During the war attempts were made in Germany to produce from bituminous coal at low temperatures a tar which might contain a greater amount of saturated and naphthenic hydrocarbons. The first at-

* Lunge-Köhler, Industrie des Steinkohlenteers, Bd. I.

† Lunge-Berl, III. Bd., 375.

tempts in this direction* produced a tar at 450° the specific gravity of which was less than one. The indifferent portions contained considerable illuminating oil, a little benzol, very little anthracene and naphthalene, no thiophene but about 1.7 per cent of paraffin. According to the Del Monte† process of destructive distillation it is possible by coking the coal at a low temperature to obtain a tar which is more aliphatic in character and, therefore, resembles lignite tar and petroleum more than it does coal tar. By distillation at low vacuum‡ there was obtained a tar which is less dense than water, with the odor of petroleum, containing no phenols, but considerable amounts of basic material and a mixture of hydro-aromatic hydrocarbons (C_9H_{18} to $C_{13}H_{26}$) and oxygen-containing bodies. The compounds $C_{10}H_{20}$ and $C_{11}H_{22}$ were like some isolated from Canadian crude oil. A crystalline body (M.P. 62°), a hydrocarbon, was obtained by distillation at 15 mm. By the distillation of coal from the Saar§ a tar of density 1.0 and of considerable viscosity was obtained. 28 per cent was distilled with steam. Hydrocarbons (dihydrotoluol, C_7H_{10}; dihydro-m-xylol, C_8H_{12}; dihydromesitylene, C_9H_{14}; naphthenes, $C_{12}H_{24}$ and $C_{13}H_{26}$; naphthalene, $C_{10}H_8$; dihydrofluorene, $C_{13}H_{12}$) were obtained. Low temperature tar|| showed a slight dextro-rotatory power.

On the average, the tars from German gas plants¶ showed the following composition.

		Per cent
C_nH_{2n-6}	Series (benzol and homologues)	2.50
$C_nH_{2n-7}OH$	Series (phenol and homologues)	2.00
$C_nH_{2n-7}N$	Series (pyridine and quinoline bases)	0.25
C_nH_{2n-12}	Series (naphthalene, acenaphthene)	6.00
C_nH_n	Series (heavy oils)	20.00
C_nH_{2n-8}	Series (anthracene, phenanthrene)	2.00
$C_{2n}H_n$	Series (asphalt, soluble components of pitch)	38.00
$C_{3n}H_n$	Series (carbon, insoluble components of pitch)	24.00
Water, ammoniacal		4.00
Gases (loss on distillation)		1.25
		100.00

* J. Gasbel., **49**, 627, 667 (1906).
† Braunkohle, **11**, 607 (1912).
‡ Berichte, **46**, 3342 (1913); **48**, 926 (1915).
§ Chem. Ztg., **40**, 211 (1916).
|| Berichte, **50**, 111 (1917).
¶ G. Kraemer, Jour. f. Gasbelencht., **34**, 225 (1891).

The above analyses were obtained with horizontal or inclined retorts. The use of vertical retorts has a decided effect on the composition of the tars. The following comparison* of results with the same coal is interesting:

	Vertical retorts	Inclined retorts
Water	5 70	10 35
Light oil to 100°.	8 90	1 00
Light oil 100° to 170°	1 20	1 60
Middle oil 170° to 230°	13 50	7 50
Heavy oil 230° to 270°	7 30	10 27
Anthracene oil over 270°	29 30	18 80
Pitch	34 10	58 13

An exact compilation of all components discovered or suspected as present in coal tar is found in Lunge-Köhler, page 221.

The undistilled coal tar is used for fuel in heating the gas retorts, in the preserving of wood, in the manufacture of roofing-felt, as an addition to natural asphalt (detection, see page 267), in the manufacture of lampblack, etc. By distillation over a free flame or by means of steam, as is known, a large number of products are obtained; these are of great importance in the preparation of dye-stuffs and of pharmaceutical products. The amounts of the different fractions obtained in the distillation are shown on page 327.

Coke-oven tars are more mobile than gas tars, and do not contain more than 10 to 12 per cent of free carbon, often only 2 to 6 per cent. According to Spilker† the tars from the coke ovens of the Ruhr district showed the following composition (sp. gr. 1.145 to 1.191):

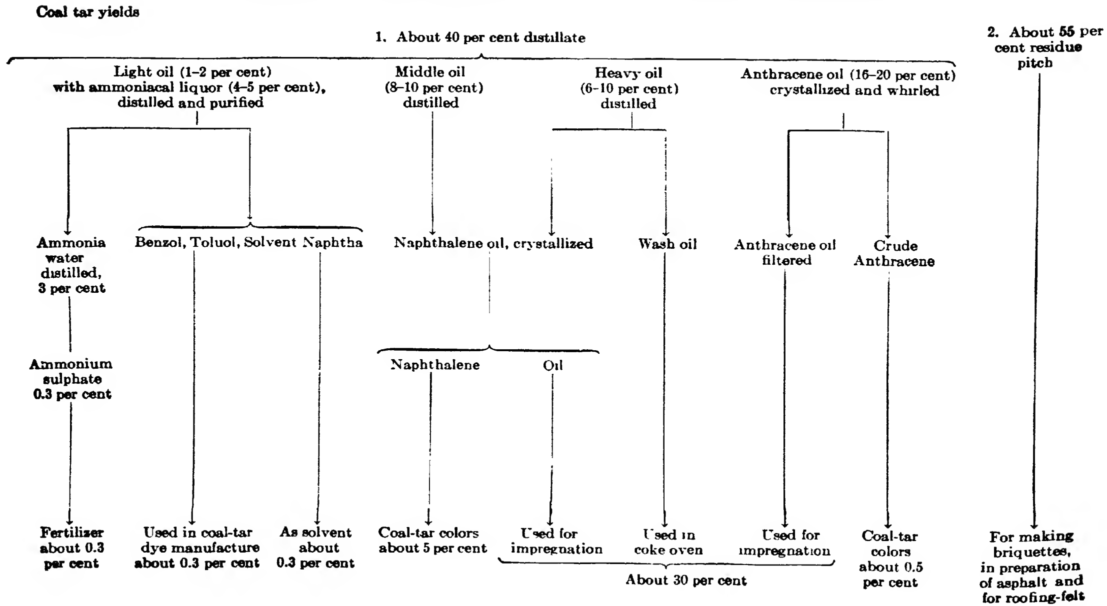
	Per cent
Water	2 69
Light oil	1.38
Middle oil	3.46
Heavy oil	9.93
Anthracene oil	24 76
Pitch	56 44
Loss	1.34

Blast-furnace tars are obtained mostly in Scotland where, instead of using coke, bituminous coal is charged into the furnace. They con-

* Schäfer, Einrichtung und Betrieb eines Gaswerks, Munchen, 1909, 194.

† Kokerei und Teerprodukte.

According to the Experience of a Coal Tar Company at Meiderich



tain more acid oils than does coal tar (phenol, cresol and especially the higher homologues), less benzol and aromatic hydrocarbons, on the other hand, more paraffin. The high ash content (flue dust) makes the pitch very much less valuable. The composition of such a tar* is given:

	Per cent	Specific gravity
Water (ammoniacal)	32 3	1 007
Oil up to 230°	2 8	0 899
Oil from 230° to 300°	7.1	0 971
Oil from 300° to solidification of the distillate	13 5	0 994
Soft paraffin	17 3	0.987
Coke	21.5	...
Loss	5 5	...

The tar obtained in water gas manufacture is similar to coal tar. (See page 152.) The crude tar contains up to 30 per cent of neutral water from which it is freed only with difficulty. According to Lunge† this tar is less valuable because of its content of paraffin. A tar from water gas carburetted with Russian crude oil had the following composition‡:

	Per cent
Benzol	1 19
Toluol	3 83
Light paraffins	8 51
Solvent naphtha	17 96
Phenols	traces
Middle oils	29.44
Heavy oils	24.26
Naphthalene	1 28
Crude anthracene	0.93
Coke	9.80
	97 20

Water-gas tar generally contains only traces of free carbon and consists in general of undecomposed gas oil, as well as aromatic decomposition products of the same. When distilled industrially, the following yields are obtained:

* Smith, Jour. Soc. Chem. Industry, **1883**, 495.

† Lunge-Köhler, 200.

‡ Mathews and Goulden, Gas World, **16**, 625; Wagner-Fischer, Jahresbericht, **1892**, 77.

	Per cent
Light and middle oils up to 230°	About 22
Heavy oils up to 300°	30
Anthracene oils over 300°	13
Pitch (very lustrous and mobile)	30
Water and loss	5

Oil-gas tar is similar to coal tar in properties and composition but differs in having a lower specific gravity and in its almost complete lack of phenol-like and basic substances. It has about the same color as coal tar but is more mobile. The amount of free carbon is about 20 per cent. Scheithauer gives the following analysis of a gas oil obtained as a product of the Thüringian brown-coal tar industry:

	Per cent
First runnings from 70° to 150°	5 to 10
Light oil from 150° to 200°	5 to 10
Middle oil from 200° to 250°	20
Heavy oil from 250° to 300°	20
Anthracene oil over 300°	30
Pitch and loss	10

Würth* found in an oil-gas tar of the same region the following composition:

	Per cent
Benzol	1.00
Toluol	2.00
Xylol	1.30
Resinifiable oils under 150°	1 00
Oil from 150° to 200°	1 50
Oil from 200° to 300°	26.60
Oil from 300° to 360°	12.60
Naphthalene	4.90
Crude anthracene	0 58
Phenols	0 30
Bases	trace
Asphalt	22 00
Free carbon	20.50
Water (neutral)	4.00

* Dissertation, Munchen, 1904.

II. Examination of the Crude Tars

(*a*) **Specific Gravity.** This must be determined in a manner somewhat different from that used for oils (page 2). The water content of the tar must be considered.

To separate the mechanically admixed water, the tar is placed in a large covered beaker and allowed to stand in warm water (not over 50°); the water collecting on the surface is poured off or removed by touching with filter paper. The tar, freed from water, is then allowed to stand at room temperature. Since at this temperature the tar is generally too viscous for the specific gravity to be determined with a pycknometer, Lunge* advises the use of a small weighing bottle (Fig. 122), in the glass stopper of which a small groove is filed at *a* (2 mm. wide and 2 mm. deep).

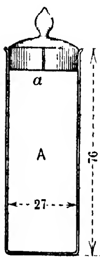


Fig. 122.

The actual weight (*a*) is first determined; the vessel is filled with water at 15° and again weighed (*b*). After emptying and drying, it is two-thirds filled with tar and kept for 1 hour in warm water (without cover) to remove all air bubbles from the tar. It is allowed to cool and is then weighed (vessel + tar = *c*). It is then filled with water, the cover put on and the apparatus allowed to stand at constant temperature. After removing the water which squeezes out through the groove, and drying, it is again weighed (*d*). The specific gravity sought is calculated as follows:

$$\frac{c - a}{b + c - (a + d)} = \text{specific gravity.}$$

(*b*) **Determination of the Free Carbon.** The method of Köhler† is used:

10 grams of tar, 25 grams of glacial acetic acid and 25 grams of toluol are boiled under a reflux condenser and the liquid is filtered through two weighed papers folded together. The papers are washed with hot toluol till the filtrate runs through colorless, and then are dried at 120° to constant weight. The difference in weight is the amount of free carbon.

The amount of free carbon gives useful information regarding the yield of pitch and also helps decide whether the tar is workable; the higher the carbon content, the greater the danger of boiling over in distillation.

(*c*) **Water.** Various‡ methods are available for the determination of water but these need not be described, since the distillation with toluol (Marcusson-Hofmann, page 72) will lead to the result.

(*d*) **Distillation Test.** See page 334 as well as Lunge-Köhler, page 499.

* Zeit. f. angew. Chem., 7, 449 (1894).

† Ding. Poly. Journ., 270, 233.

‡ Lunge-Berl, Bd. III, 386.

III. Examination of the Crude Distillates and Residues

The crude tar is separated into the following fractions by distillation:

Light oil up to 170°.
Middle oil from 170° to 230°.
Heavy oil from 230° to 270°.
Anthracene oil to the end of the distillation.
Coal-tar pitch (the undistilled residue).

The middle oil is allowed to stand and is then artificially cooled, the naphthalene being separated by filtering and pressing; the heavy oil is similarly treated and the crude naphthalene obtained is added to that obtained from the middle oil fraction. The anthracene is obtained in the same way from anthracene oil; the oil, after being allowed to stand for 3 to 4 days (it crystallizes very slowly) is filtered through linen and pressed.

(*a*) **Light Oil.** This is yellow to dark brown in color, very mobile, with a specific gravity 0.910 to 0.950; 90 per cent distills below 200°. The fraction generally begins to boil between 80 and 90°; 30 to 50 per cent distills below 120° (limit for the benzol for anilin); 50 to 80 per cent below 160° (limit for the xylols) and the rest, up to 90 per cent, between 170° and 230°. Light oil from coke oven tar frequently contains much higher boiling components.

1. **Test for Phenols.** (*a*) 100 c.c. of oil are shaken with 100 c.c. of sodium hydroxide solution of specific gravity 1.100. Each cubic centimeter increase in volume of the alkali solution may be said to be approximately equal to 1 per cent of acid oil. For a more exact determination the alkaline layer is separated from the oil, evaporated on a water bath, till no further milkiness results on the addition of water, acidified with hydrochloric acid on cooling, and salted out with sodium chloride. The volume of the separated phenols is measured, every cubic centimeter corresponding to 1 per cent. The mean of the methods will give the true content of acid oil.

(*b*) **Test for Organic and Inorganic Acids.** 50 c.c. of neutral oil, mixed with 50 c.c. of benzol, are shaken with 25 c.c. of caustic soda solution (of sp. gr. 1.15) in a cylinder graduated in 0.5 c c. divisions. The decrease in volume gives the amount of acid oils. Alcoholic soda solution is not used; action on nitriles and organic sulphur derivatives is thus avoided.

2. **Test for Bases.** The oil extracted with sodium hydroxide in 1 (*a*) is shaken with 30 c.c. of 20 per cent sulphuric acid and the increase in volume of this determined. To determine the amount of pyridine bases present, the bases extracted with sulphuric acid are carefully set free with sodium hydroxide solution (sp. gr. 1.4) in large excess. The mixture is then distilled till the pyridine can no longer be tasted; the distillate of about 50 c.c. is diluted to 200 c.c. with alcohol, and of this,

10 c.c. are treated with 50 c.c. of absolute alcohol and about 2 c.c. of a saturated aqueous solution of cadmium chloride. After standing 24 hours, the separated white crystals of the pyridine derivative are caught on a weighed filter, dried at 100° and weighed. 100 parts of the pyridine derivative correspond to 46 parts of pyridine.

The pyridine may be determined volumetrically* by dissolving the sample in 90 per cent alcohol, precipitating the pyridine with alcoholic cadmium chloride solution (as $CdCl_2 \cdot C_5H_5N$) and titrating the excess of chloride ion with $\frac{N}{10}$ silver nitrate solution.

(*b*) **Middle Oil.** This is solid or semisolid at ordinary temperatures because of the naphthalene, completely liquid at 40°, and of a yellow to brown color; the specific gravity is about 1.02; at least 90 per cent should distill below 260°. The oil pressed off from the naphthalene should distill below 250° and should have a specific gravity of 0.99 to 1.01. Middle oil contains about 40 per cent of naphthalene, 25 to 35 per cent phenols, some methyl naphthalene, as well as 5 per cent of basic substances (pyridine, quinoline, quinaldine). The testing for naphthalene by pressing has already been mentioned on page 331.

(*c*) **Carbolic Oil.** This has a specific gravity of 1.00 to 1.005, is pasty at room temperatures and boils between 160° and 250°. It contains from 25 to 40 per cent of phenols, about the same amount of naphthalene and 7 per cent of bases.

To Test for Phenols at least 500 c.c. of carbolic oil are extracted with sodium hydroxide solution (sp. gr. 1.1); the alkaline solution is distilled on a sand bath with steam till the distillate is clear and nearly odorless and tasteless. The phenols are precipitated by carbon dioxide, or dilute sulphuric acid, and saturated sodium chloride solution, washed once with water and then carefully separated from this. The product is to be examined for the amount of water contained and solidification point; a test should be made to see if it dissolves in water, forming a clear solution.†

One gram of phenol is soluble‡ in 8 to 9 grams of kerosene, 20 to 21 grams of naphtha, 40 to 50 grams of vaseline oil, or 23 to 24 grams of vaseline.

(*d*) **Heavy Oil** is a semiliquid mass of specific gravity 1.04; the most of it distills between 200° and 300°. It contains 14 to 16 per cent naphthalene, acenaphthene and similar hydrocarbons, 8 to 10 per cent acid oils (cresols and their homologues), 6 per cent of pyridine bases and 70 per cent of liquid hydrocarbons of unknown constitution.

* Chem. Zentrallblatt, II, 952 (1914).

† See also Lunge-Berl, Bd. III, 400.

‡ Pilcher, Am. J. Pharm., **86**, 149 (1914).

(*e*) **Naphthalene Oil I** boils between 180° and 230°; on cooling, 40 per cent of naphthalene separates; it contains 15 per cent of acid oils and up to 30 per cent of basic components.

Naphthalene Oil II boils between 200° and 280°; the crude naphthalene obtained from it is contaminated with some acenaphthene and some methyl naphthalene. After separating the naphthalene, there is obtained from the naphthalene oil I commercial carbolic acid; from naphthalene oil II, there is obtained creosote oil, which, mixed with an equal amount of filtered anthracene oil, is used for impregnation.

(*f*) **Anthracene Oil** is greenish yellow to green brown, has a specific gravity of about 1.1 and boils between 280° and 400°. It contains 2.5 to 3.5 per cent of pure anthracene, some phenanthrene, carbazole, fluorene, acridine and 6 per cent of phenols of unknown constitution. For a method to determine the amount of pure anthracene present in an anthracene oil and in crude anthracene see page 267. For tests for methyl anthracene, phenanthrene, carbazole and paraffin see Lunge-Köhler, page 621.

(*g*) **Pitch** is a resinous material, dark brownish black in color and giving a peculiar fracture. The specific gravity depends on its origin: from water-gas tar not over 1.20; vertical-retort-tar pitch and coke-oven-tar pitch 1.25 to 1.275; gas-tar pitch 1.30 to 1.33. Soft pitch softens at 40° and melts at 50°; medium hard pitch softens at 60° and melts at 70°; hard pitch softens at 80 to 85° and melts at 90° to 100°.

IV. Commercial Benzols

The first two fractions obtained in the distillation of coal tar consist mostly of benzol and its homologues; that portion distilling between 120° and 170° is known as solvent naphtha. The benzols found on the market are known as 90 per cent benzol, 50 per cent benzol, 30 per cent benzol and 0 per cent benzol, according to the per cent distilling below 100°. The 0 per cent benzol is pure toluol. 90 per cent benzol is used in carburetting coal and water gas; heavy benzol (solvent naphtha) is used in the rubber and varnish industry as a solvent, as well as a fuel in explosion motors. In Table 79 will be found a tabulation of the commercial products with their boiling limits and specific gravities. See page 340.

Three grades of Xylol are used:

Crude xylol	90 per cent distills between 120 and 150°
Purified xylol	90 per cent distills between 120 and 145°
Pure xylol	90 per cent distills within 3.5°
	95 per cent distills within 8.5°

TABLE 79

Factory designation	Trade names	Boiling limits	Specific gravity $\frac{15}{15}$° C.
Commercial benzol I	90 per cent benzol	90% under 100° 100% below 120°	0 880–0 883
Commercial benzol II	50 per cent benzol	50% under 100° 90% below 120°	0 875–0 877
Commercial benzol III	0 per cent benzol	0% under 130° 90% below 120°	0 870-0 872
Commercial benzol IV		30% under 130° 90% below 141.5°	. .
Commercial benzol V	Solvent naphtha I	0% under 130° 90% below 160°	0 870-0 880
Commercial benzol VI	Solvent naphtha II	0% under 145° 90% below 175°	0 880-0 910
Commercial heavy benzol	Heavy benzol	0% under 160° 90% below 195°	0 920–0 945
Pure benzol	80/81% benzol	95% boiling within 0 8°	0 883–0 885
Benzol, thiophene-free	....	95% boiling within 0 8°	0 883–0 884
Toluol......... . .	Pure toluol	95% boiling within 0 8°	0 870–0.871
Xylol......	Pure xylol	0% under 136° 90% below 140°	0 867-0 869
Cumol	. . ..	0% under 163° 90% below 172°	0 886–0 890
Pseudocumol	.. . . . .	0% under 167° 90% below 170°	0 888–0 890

The composition of commercial benzols is given by Kraemer and Spilker as follows (Table 80):

TABLE 80

	90 per cent benzol	50 per cent benzol	0 per cent benzol	Solvent naphtha, 160°	Solvent naphtha, 175°	Heavy benzol,
Benzol....	84	43	15		.	.....
Toluol..........	13	46	75	5	...	. ...
Xylol.....	3	11	10	70	35	5
Cumol..............	....	....	... .	25	60	80
Neutral naphthalene oil.......	....	. ..	....	... .	5	15

The following tests are to be made with benzols and with solvent naphtha:

(*a*) **Distillation Test.** The apparatus of Kraemer and Spilker, shown in Fig. 123, is used. The still of 150 c.c. capacity is made of 0.6 to 0.7 mm. copper. The dimensions in general are shown in the diagram. The thermometer bulb reaches into the middle of the bulb of the distilling column. The neck of the flask is 25 mm. long, 22 mm. wide at the top and 20 mm. at the bottom. 100 c.c. of sample are distilled.* The temperature at which the first drop falls from the adapter is taken as the beginning of distillation; the rate of distillation is so adjusted that 5 c.c. pass per minute (2 drops per second).

* The apparatus may be obtained from Dr. R. Muencke, Berlin, Luisenstrasse.

The distillation is ended when 90 per cent (or with pure products 95 per cent) has passed over. The following fractions are to be caught:

With pure benzol	Up to 79°	First runnings
	79–81°	benzol
	residue	
50 and 90 per cent benzol	Under 79°	First runnings
	79–85°	benzol
	85–105°	intermediate fraction
	105–115°	toluol
	residue	xylol
Toluol	Under 109°	First runnings
	109–110.5°	toluol
	residue	
Xylol	Under 135°	First runnings
	135–137°	p-xylol
	137–140°	m-xylol
	140–145°	o-xylol
	residue.	

(*b*) **Test for Carbon Disulphide.** 90 per cent commercial benzol contains 0.2 to 1 per cent of carbon disulphide.* The specific gravity of benzol is increased by the carbon disulphide† (0.0033 by 1 per cent by volume, 0.0065 by 2 per cent by volume).

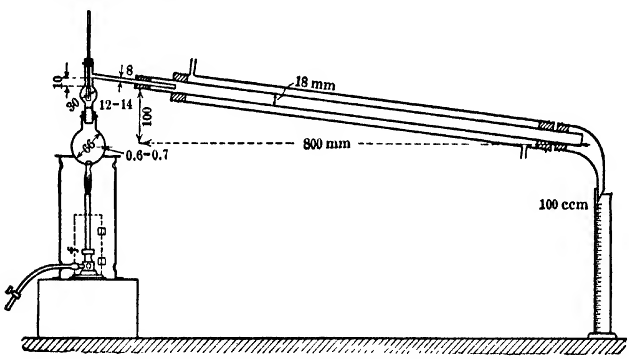


Fig. 123.

The qualitative detection of carbon disulphide is best made by the method of Liebermann and Seyewetz.‡ 10 c.c. of the sample are treated with 5 drops of phenylhydrazine and, with frequent shaking, are allowed to stand for 1.5 hours. Even when only 0.03 per cent of carbon disulphide is present, a visible precipitate of phenylhydrazine phenylsulphocarbazinate will form. The test can be made even more delicate by first distilling the benzol and examining the more volatile portions for carbon disulphide.

* Muspratt, **1908**, 46.

† Nickels, see Scluhtz, Steinkohlenteer, Bd. I, 37.

‡ Ber., **24**, 788 (1891).

More rapid than this is the detection by the Votoček and Potemšil* modification of the Hofmann reaction:

$$CS_2 + 2\ C_6H_5NH_2 \longrightarrow CS\ (NH \cdot C_6H_5)_2 + H_2S.$$

This takes place rapidly in alkaline solution; the alkali sulphide formed can be easily and certainly detected by means of sodium nitroprusside.

The amount of carbon disulphide may be quantitatively determined by the method of Frank† by shaking the sample with alcoholic potash and titrating the potassium xanthogenate with copper sulphate (Hofmann xanthogen reaction).

50 grams are mixed with 50 grams of alcoholic potash (11 grams in 90 grams of absolute alcohol) and are left several hours at room temperature. The mixture is then shaken with 100 c.c. of water, the aqueous layer is separated and the benzol repeatedly washed with water. The wash waters are to be united with the first solution containing xanthogenate. All or an aliquot part of the solution is then titrated with copper sulphate (12.475 grams crystallized copper sulphate per liter, 1 c.c. being equivalent to 0.0076 gram of carbon disulphide). The solution is neutralized with acetic acid and then copper sulphate added till a drop of the solution on filter paper gives a red-brown zone when touched with a drop of potassium ferrocyanide. The end-point of the titration is also shown by the clumping together of the at first finely divided precipitate of copper xanthogenate. When more than 5 per cent of carbon disulphide is present (as is the case in the first runnings of benzol) more alcoholic potash, or less of the sample, should be used. The higher "benzols" are free from carbon disulphide.

(*c*) **Thiophene.** 1. From 0.05 to 0.5 per cent is present in the commercial benzols. In a porcelain dish rinsed out with pure sulphuric acid, a few c.c. of concentrated sulphuric acid are poured on a few grams of isatin, covered with benzol, and are then allowed to stand covered with a watch glass. Blue rings form about the isatin (indophenin) when thiophene is present. The reaction is not given by pure benzol.

2. Thiophene is quantitatively determined by a colorimetric method.‡ The test solutions are made up with absolutely pure benzol and pure thiophene (Kahlbaum) in concentrations of 0.5, 0.1, 0.075, 0.05, 0.025 and 0.01 per cent. 25 c.c. of isatin-sulphuric acid (0.5 gram in 1000 grams of pure concentrated sulphuric acid) are put into a 100-c.c. measuring flask, 25 c.c. of pure concentrated sulphuric acid added and then 1 c.c. of the sample to be tested; to a second isatin-sulphuric acid mixture 1 c.c. of test benzol is added. The solutions are shaken for 5 minutes and then their colors compared against a white background after 15 minutes. Commercial benzol is tested from 0.5 per cent down; pure benzols from 0.25 per cent down. In a closed vessel 0.05 per cent can be detected; in an open porcelain dish the method is accurate to within 0.01 per cent if for every 25 c.c. of 0.05 per cent isatin solution 1 c.c. of test benzol or 1 c.c. of sample is added.

3. Benzol§ may be boiled with HgO and 2 volumes of glacial acetic acid for 15 min. under a reflux condenser. The precipitate is filtered, washed with ether and

* Chem. Ztg. Rep., **15,** 275 (1891).

† Chem. Ind., **1901,** 262.

‡ Schwalbe, Lunge-Köhler, 972.

§ Chem. Umschau., **23,** 62 (1916).

then dried. It has the composition $C_4S(HgC_2H_3O_2)_4$. The thiophene-content can thus be calculated.

(*d*) **Unsaturated Compounds.** If a dark brown color develops on shaking concentrated sulphuric acid (94 per cent) for 5 minutes with an equal volume of benzol, the presence of unsaturated bodies (cumarone, indene, etc.) is indicated. The ability to absorb bromine has been used to determine these unsaturated bodies quantitatively.

(*e*) **Paraffin Hydrocarbons.** The specific gravity of the benzols (0.87 to 0.89) is decidedly reduced by the presence of naphtha (sp. gr. 0.65 to 0.75). For the approximate determination of naphtha in the presence of benzol and solvent naphtha, the behavior in the presence of nitric acid is no longer used.

According to Kraemer and Spilker 200 c.c. of the sample are shaken with 500 c.c. of fuming sulphuric acid (containing 20 per cent of SO_3) in a roomy separatory funnel for 15 minutes, avoiding heating. After standing 2 hours, the used sulphuric acid is drawn off and the operation twice repeated. Hydrocarbons, with the exception of paraffins and naphthenes, and carbon disulphide are destroyed. The combined acid extracts are poured on about the same weight of finely powdered ice, with frequent shaking to avoid heating above 40°. The undissolved hydrocarbons are then distilled over a free flame until 50 c.c. of water, besides the oil originally passing, have distilled. In this way all dissolved or mechanically enclosed oil is collected, and, after drawing off the water, united with the original oil. Then the total amount of oil is shaken with 30-gram portions of sulphuric acid (fuming, 20 per cent SO_3) till no more change of volume takes place. The number of grams of oil is to be divided by 2 to find the per cent of paraffin hydrocarbons present.

90, 50 and 0 per cent benzols rarely contain more than 1 per cent of paraffins, toluol contains none and xylol sometimes as much as 3 per cent. To distinguish between benzol and paraffin hydrocarbons, according to Holde and Valenta, see pages 125 and 201.

V. Disinfecting Oils*

(*a*) **Carbolineum.** This term includes heavy coal-tar oils for disinfecting purposes and for preserving timber. The oils are obtained by pressing crude anthracene (green oils) and then may be further treated with zinc chloride or with chlorine.† The addition of zinc chloride is supposed to replace the bactericidal action of the higher phenols which are no longer present in these portions of coal tar; the treatment with chlorine, on the other hand, causes a thickening of the oils so that the viscosity, the flash point and the specific gravity are

* Literature: Lunge-Köhler, Steinkohlenteer, Band I, 606. Muspratt, Chemie, 1896, 5, 248; 1905, 8, 60.

† D. R. P., 46,021.

raised; the chlorine also removes the unpleasant odor of the crude carbolineum. Rosin oils are frequently added to carbolineum. The mineral oil imitations of carbolineum do not have the preservative action of the anthracene oil; consequently the detection of the hydrocarbons of water-gas tar is of importance. The test with dimethyl sulphate (Valenta test, see page 201) can be made. The name should not be taken to mean that the product is carbolic acid.

TABLE 81

CARBOLINEUMS

	Avenarius* D.R.P., 46,021	Other makes*	Various makes†
Specific gravity	1 128	1 075–1.130	1.11–1 12
Viscosity at 17° C.	10 0	1 5–6 2	8–14 (b. 20°)
Flash point	131°	58–110°	106–118°
Burning point	190°	95–130°	. .
Beginning of boiling	230°	200–270°	205–240°
Distillate below 250°	0	8–53%	5–11%
Distillate 250–300°	22 6%	20–51%	77–78%
Ash	0.03%	0 02–0 83%	0.07–0.08%
Phenol	Traces	0 4–5 4%	. . .
Separation of naphthalene	None	Considerable	. . . .
Anthracene in the residue	None	Present	. . . .

* Examined by Filsinger, Chem. Ztg, **15**, 544 (1891).
† Examined in the K. Materialprüfungsamt

(*b*) **Urinal Oils.*** The following tests are to be applied:

1. The specific gravity should be less than that of the urine, that is, less than 1, in order to cover the odorous substances.
2. It should have a solidification point under − 10°.
3. Its viscosity (Engler) should not be less than 9 at 20°.
4. The phenol content should not be less than 10 liters per 100 kilograms.

(*c*) **Creosote Oil.** (This is also used as lucigen oil for street lighting.) It is obtained from the heavy oil of coal tar by fractionation and by pressing of the solids separating (naphthalene, etc.).

The oils used for preserving timber should have the following properties (as required by the Prussian State railways):

On distillation not more than 3 per cent should pass at 150°, 10 per cent at 200°, 25 per cent at 235° (bulb in vapor). Specific gravity at 15° between 1.04 and 1.1. At 40°, or on mixing with an equal volume of benzol (crystallizable), only traces of insoluble material should be observable. Two drops of the mixture (or melted oil) dropped on a filter paper should not leave a definite spot of undissolved substances.

* Bericht über die Thätigkeit des kantonalen chemischen Laboratoriums Basel-Stadt, 1904.

In some cases (as for the German-China railways) it was specified that the amount of acid (carbolic) contents soluble in sodium hydroxide of specific gravity 1.15 be at least 6 per cent (in Saxony at least 12 per cent).

Lucigen oil (tar oil for vapor lamps) should, according to the specifications of military authorities, have a specific gravity of at most 1.02 at 15°, should not contain water or mechanical impurities of any sort, or at ordinary temperature any undissolved naphthalene or similar bodies; it should not show any sediment on long standing at ordinary temperatures. Lucigen oil should be liquid at − 10°, except for small amounts of crystalline separations (naphthalene, etc.). On distillation at least 81 per cent must distill below 300°. A complete separation of the naphthalene by artificial cooling would not be profitable because of the lack of uses to which it might be put.

The methods to be used in the examination of these oils have already been described in connection with other substances.

VI. Anthracene Oils

These are the heavy-tar oils which by special treatment (heating and distillation) are thickened to the point where they may be used for lubrication. They are used for lubrication of bearings, sliding surfaces, and for axles where the pressure is not too great or the temperature extreme. They are not suitable for cylinder, steam engine or motor lubrication, but are used for shafting, ring-lubricators, pumps. See Chapter I and the section on Lubrication for tests.

VII. Wood Cement

Wood cement* is a coal tar, the viscosity and adhesiveness of which have been increased by the addition of sulphur, rosin and other substances; oil-gas tar is occasionally used. The sulphur acts as a condensing agent (at a temperature of 110°) on certain substances in the coal tar, whereby the melting point of the product is raised. It has been found desirable to add the sulphur to the heavy tar oils in a dissolved condition. Coal-tar pitch is used to thicken the less viscous coal tar; a high adhesive power is obtained by the addition of rosin and of rosin oil. To prevent the draining out of the wood cement from roofing-felt (for which it is much used) some factories mix with it marl, chalk, asphalt-rock powder or similar mineral matters.

Good wood cement† should have a pasty and glistening appearance; a matte color indicates free carbon, which may come from the use of

* Köhler, Asphalte, 246.

† Friese, Asphalt- und Teerindustriezeitung, Nos. 23, 24, 25 and 26.

the less valuable pitches, or arise from too high a temperature of preparation. Wood cement should not foam on heating, or evolve much hydrogen sulphide; these phenomena are caused by the presence of water, or are due to the fact that the sulphur was added at too low a temperature. Larger amounts of easily volatile components should not be present; furthermore it is desirable that wood cement be liquid at 90°, so that it may be applied to the materials in thin layers. Its adhesiveness should be high; two strips of paper painted with it should adhere permanently. A content of paraffin and paraffin oil is a disadvantage.

In testing the wood cement chemically, the bitumen is extracted with chloroform, the extract containing bitumen, rosin, paraffin and combined sulphur. The bitumen is separated from the latter bodies by its insolubility in absolute alcohol, the paraffin separates on cooling the hot alcoholic solution and the sulphur can be determined by the method of Graefe (page 78).

Mineral inorganic bodies, sulphur and carbon, remain insoluble on treatment with benzol; the sulphur can be extracted with carbon disulphide; the carbon can be determined by ignition of the sulphur free residue.

The melting point (Kraemer-Sarnow or Ubbelohde, pages 256, 37) is of importance in physical testing. The adhesiveness is determined by pasting two sheets of paper together and then pulling these apart on a machine similar to the cement testers, the force being measured in terms of the weights applied.

The covering power is determined with a small short-haired stiff brush; it should leave a smooth surface with no streaks.

VIII. Cumarone Resins

Cumarone resins are polymerization and in part condensation products of cumarone and indene, as well as of other unsaturated portions of crude benzol. After removal of the acids used in washing, the residue is neutralized and distilled, the cumarone resin remaining as a residue in the still. These resins are pale yellow to dark brown, of different degrees of hardness and with a considerable range in melting point. They have a peculiar odor.

They are indifferent to alkaline liquids (5 per cent soda solution, 1 to 5 per cent of caustic soda, or 10 per cent ammonia) though prolonged attack with 5 per cent sodium hydroxide is effective. Treatment with alcoholic sodium hydroxide does not cause saponification.

These resins do not dissolve in 90 per cent, or absolute alcohol, or in linseed oil to any great extent. They are soluble in benzol, ether, tetrachloride of carbon, trichlor-ethylene, and are somewhat less soluble in naphtha and in turpentine; soft resins are readily soluble however in naphtha and in turpentine. Painted on strips of metals, on evaporation of the solvent, there are left amber-yellow to red brown, shining deposits which have considerable elasticity and do not crack on bending back and forth; when scratched with a steel needle, a smooth straight depression is produced. These materials* are suited for varnishes.

All these substances give a positive Storch-Morawski reaction so that this test cannot be used to detect colophony in cumarone resin. The acid value is 1.2 to 5.8, the saponification value, 5.1 to 11.8. The acids which are difficultly soluble in petroleum ether are more soluble in the presence of fatty acids. On heating for 1 hour they become less soluble in petroleum ether, the acid value decreases, while the saponification value is hardly altered. The cumarone resin acids are easily separated from fatty or rosin acids because of their slight solubility in petroleum ether. Cumarone resin can be identified by isolating the non-volatile unsaponifiable components which boil at 160 to 220° and have a characteristic odor.

The cumarone resins which were formerly considered worthless and burned as fuel were used in Germany from shortly after the outbreak of the war with great success as substitutes for linseed oil varnish, colophony, and other resins. Their use for painting wood had long been recommended. Although they are not ideal substitutes for linseed-oil varnishes and resins they have met the somewhat lessened standards and will undoubtedly find more use in the future. Thirty different varieties are now recognized.

Tests

1. **Color.** The color of the resin cannot well be compared with a standard. The color of a benzol solution of the resin is therefore compared with a solution of potassium bichromate.

1.5 grams of potassium bichromate are dissolved in 100 c.c. of 50 per cent sulphuric acid. 1 to 1.5 grams of resin (weighed to 0.1 gram) is dissolved in enough benzol to give 0.1 gram resin per cubic centimeter (in some cases the strength should be 3.5 or 5 per cent). In identical comparison tubes the clearness or transparency but not the color of the solutions is compared. With dark resins a 50-candle power

* Kraemer and Spilker, Ber., **23**, 78, 3276 (1890). Störmer and Böes, Ber., **33**, 3013 (1900), Bottler, Kunststoffe, **5**, 277 (1915). Krumbhaar, Farbenztg., **21**, 1086 (1914). Also Farbenztg., **22**, 917, 945 (1915); **23**, 307 (1916). D. R. P. 270993; 281432.

lamp is used as source of light, usually the tubes are held against the sky. Pale to light brown resins in 10 per cent solutions are more transparent than the bichromate solution, light brown to brown resins in 3.5 per cent solution must not be darker; brown to dark must in 10 per cent solution allow light to shine through from the 50-candle power incandescent, while a dark to black resin must allow it to gleam through a 5 per cent solution; a black resin does not allow light from an incandescent to gleam through a 5 per cent solution.

2. **Hardness and Consistency.** (*a*) This is usually determined by the method of Kraemer-Sarnow (page 256). Brittle resins have a softening point above 50°, hard resins between 40 and 50°, medium hard between 30 and 40°.

(*b*) For soft and viscous resins may be used the nail test. For this purpose are used 5 inch wire nails weighing 23 grams ± 1. The resin (in a vessel of 10 cm. diam.) should be in a layer about 20 cm. thick. The nail is allowed to penetrate by its own weight, the time of penetration to the head, being measured in seconds; it may be kept from falling to one side by means of a wire loop.

As a dividing line between a medium-hard and soft resin may be taken a (Kraemer-Sarnow) softening temperature of 30°, between soft and viscous, a penetration time by the nail of 500 seconds, between viscous and liquid, a nail test of 100 seconds.

3. One hundred grams of the sample are heated in a 350 c.c. glass retort in an oil bath to 150°, 50 c.c. of benzol being added to avoid foaming. Dry steam is passed in until the temperature of the oil bath is 260 to 270°; this requires about 1 hour. The residue is weighed.

If the residue is less than 35 per cent, then the substance heated must be considered as a cumarone resin-containing residue or oil. This test is necessary only when the nail test gave a penetration time of 5 seconds or less.

4. **Detection of Foreign Materials.** A ten per cent solution of the resin is treated with the same volume of concentrated sulphuric acid without heating; pure resins show no changes. Adulterated resins show precipitates, especially after diluting with 2 volumes of water.

IX. Phenol Condensation-Products

Phenol* and formaldehyde react to form synthetic resins (like Bakelite) on heating with catalytic agents such as acids (Lebach) or alkalies (Baekeland) or salts, or even without catalysts. When casein, dissolved in cresol, is heated with formaldehyde under 3 to 4 atmos-

* Baeyer, Ber., **5**, 1095 (1872); **19**, 3004, 3009 (1886); **25**, 3477 (1892); **27**, 2411 (1894). Kleeberg, Lieb. Amalen, **263**, 283 (1891). Baekeland, Chemiker Ztg., **33**, 317, 326, 347, 358 (1909). Also Kunststoffe, **5**, 196 (1915); **6**, 45 (1916).

pheres pressure, resins, which are soluble in alcohol, are formed. On prolonged heating or at higher pressure, insoluble resins are produced. The alcohol-soluble resins are not soluble in drying oils, so are used only as substitutes for shellac in the manufacture of spirit varnishes. The resins have a phenol-like odor, which disappears only slowly but more rapidly on heating; because of this liberation of phenol, they act as antiseptics, but darken and take on a reddish color. The resins are stable in air and act better on wood than on metal; the wood seems to hasten the hardening.

Resins resembling copal have been produced by the action of natural resins, oils, cumarone resins and other bodies on phenol resins; they are said to be good substitutes. They are dark yellow to red brown, transparent, glistening, odorless, resinous. Some begin to melt at 120 to 160°, others melt at 180 to 260°. They are not soluble in alcohol, naphtha, or kerosene; they are soluble (or nearly so) in acetone, benzol, trichlorethylene, carbon tetrachloride, and in linseed oil at 280 to 310°.

Resins may also be made in which benzyl-chloride, naphthalene sulphonic acids and phthalic acid anhydride are components.

By condensing aryl-oxy acetic acids with formaldehyde in the presence of hydrochloric acid as a catalyst synthetic resin acids are obtained.* The product is yellow and very hard, and because of its acidic nature it is soluble in sodium or ammonium hydroxide; it also dissolves in acetone.

On applying the Graefe diazobenzol test (page 268) to alkaline extracts of the phenolic resins, a positive test is obtained.

Other tests depend on the use to which the resin is put. Solubility in alcohol, benzol, solvent naphtha, or tendency to dry, resistance to atmosphere of thin layers (see page 491), insulating power and other practical tests, are applied.

* Chem. Ztg., **40**, 725 (1916).

CHAPTER VI

Vegetable and Animal Fats and Oils

I. Composition

The saponifiable fats and oils obtained from plants and animals are glyceryl esters of saturated and unsaturated acids; these esters can be hydrolyzed into glycerine $C_3H_5(OH)_3$ and fatty acids, generally containing an even number of carbon atoms, such as oleic acid $C_{18}H_{34}O_2$, stearic acid $C_{18}H_{36}O_2$, palmitic acid $C_{16}H_{32}O_2$, linoleic acid $C_{18}H_{32}O_2$, and linolenic acid $C_{18}H_{30}O_2$. These esters are called " glycerides."

The glyceryl radical is united in the fats with three similar acid radicals, as in tri-stearin $C_3H_5(C_{18}H_{35}O_2)_3$ and triolein $C_3H_5(C_{18}H_{33}O_2)_3$, or with several different radicals, as in mixed esters, such as oleo-distearin $C_3H_5(C_{18}H_{33}O_2)(C_{18}H_{35}O_2)_2$ or $C_3H_5(C_{18}H_{33}O_2)(C_{16}H_{31}O_2)(C_{18}H_{35}O_2)$ oleo-palmito-stearin.

In the non-drying oils (olive, almond, peanut, bone, neat's-foot) glycerides of acids with some unsaturated linkings occur; in the semi-drying oils (cottonseed, sesame, kapok, corn) glycerides of more unsaturated acids together with the glycerides of oleic acid are present; while the drying oils (linseed, hempseed, poppyseed, sunflower, tung) contain glycerides of extremely unsaturated acids (linoleic, linolenic) together with olein. The physical and chemical properties of the oils are determined by their components. See Tables from page 422 on. In all these oils there occur liquid glycerides and varying amounts of glycerides of solid acids (palmitic, stearic, arachidic) besides differing quantities of solid fatty acids themselves. For special purposes where acids or solid components might interfere (neat's-foot oil for torpedo lubrication), the acid is separated by treatment with alkali and the solid glycerides by pressing cold. In the solid fats, glycerides of the solid fatty acids (palmitic and stearic) predominate.

The waxes (page 513) are not glycerides but esters of acids of high molecular weight (palmitic, cerotic, myricylic) with monoatomic water-insoluble alcohols of high molecular weight (cetyl $C_{16}H_{34}O$, myricyl $C_{30}H_{62}O$). Cetine is cetyl palmitate. Many waxes (beeswax) contain free fatty acids and solid hydrocarbons. The waxes do not give water-soluble soaps, as the alcohols and hydrocarbons separate from

the soap solutions. Liquid waxes however contain alcohols insoluble in water but soluble in soap solutions.

(a) *Glycerides*

Based on the work of Chevreul* the assumption was made, up to a few years ago, that the essential components of fats were triglycerides in which the glyceryl radical was united with three similar acid radicals; however, many mixed glycerides (see Table 82) have been recently discovered (in cow's butter, cacao butter, lard, mutton tallow and elsewhere†). In old fats di-glycerides are sometimes found; for example, dierucin $C_3H_5(C_{22}H_{41}O_2)_2OH$ occurs in old rapeseed oil,‡ being perhaps formed with separation of erucic acid when the oil becomes rancid. Marcusson,§ however, was unable to find any lower glycerides in rancid fats.

TABLE 82

MIXED GLYCERIDES IN FATS

Origin	Name of mixed glyceride	Melting point °C.
Butter	Oleo-palmito-butyrin	15.5
Mkani fat	Oleo-distearin	44
Lard	α-Palmito-distearin	68 5
Beef fat	β-Palmito-distearin	63 3
Beef fat	Stearo-dipalmitin	50 and 60
Cocoa butter	Caprilo-lauro-myristin	13 to 15
Cocoa butter	Myristo-dilaurin	33
Cocoa butter	Lauro-dimyristin	37 5
Cocoa butter	Palmito-dimyristin	45
Linseed oil	Dioleo-stearin	.
Linseed oil	Linoleo-distearin	32
Mutton tallow	Palmito-distearin	57 5

* Les gras d'origine animale, Paris 1815–23. New Edition, 1889.

† Heise, Arbeit. a. d. k. Gesundheitsamt, **1896**, 540; **1897**, 306; Chem. Umsch., **6**, 91 (1899); Henriques and Künne, Chem. Umschau., **6**, 45 (1899); Blyth and Robertson, J. Chem. Soc., **55**, 162 (1889); Klimont, Ber., **34**, 2636 (1901); Fritzweiler, Arbeit. a. d. k. Gesundheitsamt, **18**, 371 (1901); Kreis and Hafner, Ber., **36**, 2766 (1903); Okada, Chem. Ztg., **32**, 1199 (1908); Holde and Stange, Ber., **34**, 2402 (1901); Ubbelohde and Marcusson, Ber., **38**, 1247 (1905); A. Bömer, Ztsch. f. Unt. d. Nahr. u. Gen. Mitt., II, 90 (1907); **17**, 353–396 (1909); Hafner, same journal, **7**, 641; Hansen, Kreis and Hafner same, I, 641 (1904); **25**, 322 (1913); Meyer and Beer, Monatshefte, **33**, 311 (1912); Chem. Ztg., **37**, 890 (1913); **38**, 844 (1914).

‡ Reimer and Will, Ber., **19**, 3320 (1886).

§ Ber., **39**, 3466 (1906).

Holde* claims that the presence of mixed glycerides determines the relatively low solidification point of the liquid fats; for although olive oil contains over 15 per cent of higher melting acids, palmitic, stearic and arachidic, in the form of glycerides, the point of solidification is under 0° C.

(b) *Double Melting Point*

A characteristic of solid glycerides is the phenomenon of so-called double melting point which was first noticed by Heintz in the case of stearin. This was at first thought† to be due to the formation of different isomeric modifications, but recently Guth‡ assumed that the glycerides went into a labile condition like that of super-cooled water. According to Bömer the phenomenon is due to physical dimorphism as in the case of sulphur and of silicic acids. Since the glycerides crystallized from solvents have only one melting point, the stable modification is assumed to be present in them while the modification obtained on rapid cooling of the melted material consists of the labile form which passes into the stable condition at the so-called first melting point. The same transformation takes place gradually at room temperature. The existence of these two modifications of the glycerides which might be attributed to polymorphism, polymerism or a subtle isomerism§ has not yet been definitely explained.

(c) *Fatty Acids*

The fats contain glycerides of fatty acids (aliphatic in nature) and some small amounts of free acids; the acids except in rare and uncertain instances contain an even number of carbon atoms. Table 83 lists the more important acids identified as occurring in fats and oils.

Chevreul had assumed the existence of a margaric acid radical in natural fats but various investigators had later shown the supposed acid to be a mixture; recently, however, Meyer and Beer claim to have isolated from datura oil, by fractional crystallization of the lithium salts, an acid of the composition $C_{17}H_{34}O_2$ and melting point, 57°. This is noteworthy in view of the great preponderance in the fats of acid radicals with an even number of carbon atoms. A similar acid was also apparently found|| in horse fat, and in goose fat.

* Ber., **35,** 4307 (1902); **45,** 3701 (1912). Also Kremann and Schoulz, Monatshefte, **33,** 1063 (1912); Also **34,** 1291 (1913).

† Duffy, Jour. f pract. Chem., **57,** 335 (1852).

‡ Zeit. f. Biologie, **44,** N. F., **26,** 109 (1903).

§ Knoevenagel, Ber., **40,** 515 (1907). Also Grün, Ber., **45,** 3691 (1912).

|| Monatshefte, **33,** 311 (1912); **36,** 281 (1915).

TABLE 83

The Acids Occurring in the Glycerides

Saturated Acids of the Series $C_nH_{2n}O_2$

Formula	Name	Mol. wgt.	M.P. °C.	B.P. °C.	Occurrence	M.P. of ethyl ester °C.
$C_2H_4O_2$	Acetic	60	Solid P.	118 at 760 mm.	Maccasar oil	....
$C_4H_8O_2$	Butyric	88	+17.5 − 6.5	162 3 at 760 mm.	Butter fat	....
$C_6H_{12}O_2$	Caproic	116	Solid P <−18	199.7 at 732 mm	Butter fat Cocoanut	....
$C_8H_{16}O_2$	Caprylic	144	+16 5	237 at 760 mm.	Cocoanut	...
$C_{10}H_{20}O_2$	Capric	172	+31 4	270 at 760 mm.	Cocoanut	....
$C_{12}H_{24}O_2$	Lauric	200	47 5	102 at 0 mm.	Laurel oil Cocoanut	−10.
$C_{14}H_{28}O_2$	Myristic	228	57 5	121 at 0 mm.	Mace butter	....
$C_{16}H_{32}O_2$.	Palmitic	256	63 5	139 at 0 mm.	Palm oil Japan wax	...
$C_{18}H_{36}O_2$.	Stearic	284	69 5	155 at 0 mm. 232 at 15 mm.	Tallow	33.7
$C_{20}H_{40}O_2$.	Arachidic	312	77		Arachis	50
$C_{22}H_{44}O_2$	Behenic	340	82	.	Ben	49
$C_{24}H_{48}O_2$	Lignoceric Carnaubic	368	80 5 72 5	.. . .	Arcahis Carnaubic wax	55
$C_{26}H_{52}O_2$.	Cerotic	396	77 8		Beeswax	60
$C_{30}H_{60}O_2$.	Melissic	452	89		Beeswax	73

Acids of the Oleic Series $C_nH_{2n-2}O_2$

Formula	Name	Mol. wgt.	B.P. °C.	B.P. °C.	Occurrence
$C_5H_8O_2$	Tiglic	100	+64 5	198 5 at 760 mm.	Croton oil
$C_{16}H_{30}O_2$ ..	Physetoleic	254	+30	. . . .	Seal oil
$C_{18}H_{34}O_2$ ...	Oleic Rapic	282	+14	153	In nearly all oils Rape oil
$C_{22}H_{42}O_2$	Erucic	338	34	281 at 30 mm.	Rape oil

Acids of the Linolic Series $C_nH_{2n-4}O_2$

Formula	Name	Mol wgt.	M.P. °C.	B.P. °C.	Occurrence
$C_{18}H_{32}O_2$ ...	Linoleic Tariric Elaeomargaric	280	<−18 +50 5 43–44	.. . .	Drying oils Oil of picramnia Tung oil

		Acids of the Linolenic Series, $C_nH_{2n-6}O_2$			
$C_{18}H_{30}O_2$......	Linolenic Isolinolenic	278	.... .	... .	Linseed oil
		Acids of the Series, $C_nH_{2n-8}O_2$			
$C_{18}H_{28}O_2$	Clupanodonic	276	.	....	Fish oils
		Saturated Hydroxy-acids, $C_nH_{2n}O_3$			
$C_{16}H_{32}O_3$.	Lanopalmic	272	88	. . .	Wool wax
$C_{31}H_{62}O_3$ ..	Cocceric	480	93	. .. .	....
		Hydroxy-acids of the Castor Oil Series, $C_nH_{2n-2}O_3$			
$C_{18}H_{34}O_3$.....	Ricinoleic Ricinelaidic	298	+ 5 53	. .... .	Castor
		Saturated Hydroxy-acids, $C_nH_{2n}O_4$			
$C_{18}H_{36}O_4$......	Dioxystearic	316	142	....	Castor
		Bibasic Acids, $C_nH_{2n}(COOH)_2$			
$C_{22}H_{42}O_4$	Japanic	370	118	.. ..	Japan wax
		Cyclic Acids			
$C_{18}H_{32}O_2$	Chaulmoogric	28	68	248 at 20 mm.	Chaulmoogra oils

(*d*) *Other Ingredients of Fats*

1. Lecithins

Lecithins are found mixed with fats and oils, as in the fat of egg-yolk. These may be considered as phosphorized fats in which phosphoric acid takes the place of one of the fatty acid radicals; besides being united to the glyceryl radical the phosphoric acid is also attached to a choline radical.

$$
\begin{array}{l}
CH_2 - O \cdot CO \cdot C_{17}H_{35} \\
\;| \\
CH - O \cdot CO \cdot C_{17}H_{35} \quad (CH_3)_3N \cdot OH \\
\;| \qquad\qquad\qquad\qquad\qquad\qquad\quad / \\
CH_2 - O \cdot PO(OH)O \cdot CH_2 \cdot CH_2
\end{array}
$$

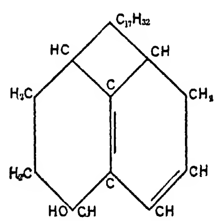
This gives the formula of a typical lecithin. The lecithins are widely distributed in nature. The above stearyl derivative is soluble in alcohol and ether and is wax-like and crystalline; it is soluble in water, forming an opalescent solution. It forms salts with acids and bases; with platinic chloride, it forms an insoluble double salt $(C_{42}H_{84}NPO_8HCl)_2$-$PtCl_4$. By boiling with acids or barium hydroxide it is hydrolyzed into choline, glycero-phosphoric acid and stearic acid. Its constitution is derived from this, and the conclusions seem justified by synthetic work.*

2. Unsaponifiable Components of Fats

(a) *Sterols*†

All vegetable and animal fats and oils contain small amounts (Table 84) of unsaponifiable bodies, alcohols and hydrocarbons; characteristic are the sterols which are used in determining the animal or vegetable origin of the fat. The sterols include cholesterin (cholesterol), phytosterin (phytosterol) and similar alcohols of high molecular weight.

(α) **Cholesterin** occurs in all animal fats, in gall-stones, and in the brain; it is an unsaturated, secondary, aromatic alcohol of the formula $C_{27}H_{46}O$. Its structural formula is indicated: —



It has a melting point of 148.5°; when crystallized from alcohol or ether it forms thin rhombic plates, containing water of crystallization. Its optical rotatory power in chloroform is $[\alpha]_D = -31.1°$. The characteristic Liebermann and Hager-Salkowski reactions are given on page 519. In ether solution, bromine gives a dibromide; it forms with digitonin a double-compound which is insoluble in most solvents ($C_{27}H_{46}O + C_{55}H_{94}O_{28}$ gives $C_{82}H_{140}O_{29}$). See page 350. With the aid of this test it is possible to detect $\frac{1}{10}$ milligram of sterin in 1 c.c. of 90 per cent alcohol.

* Hundeshagen, J. fur. prakt. Chem. [2], **28,** 219 (1883); Grün and Kade, Ber., **45,** 3367 (1912).

† Salkowski, Z. für Analyt. Chem., **1887,** 557. Bömer, Z. Nahr u. Genussm., **21,** 81, 532 (1898). Windaus, Ber., **39,** 2261 (1906); **48,** 1065 (1915); **50,** 133 (1917). Marcusson, Chem. Ztg., **41,** 577, 590 (1917).

(β) **Isocholesterin.** Occurs in wool-fat (page 519). Melting point 136 to 138°; $[\alpha]_D = +60°$. It is said* to be dihydro-cholesterin.

It may be separated (Marcusson and Meyerheim) from cholesterin by means of digitonin, since isocholesterin is not precipitated.

(γ) **Coprosterin,** found in the feces of carnivorous animals, has a melting point of 95 to 104°, is said† to be an isometric dihydrocholesterin; it is not precipitated by digitonin.

(δ) **Oxycholesterin**‡ usually is found associated with cholesterin. The melting point is not sharp; at 100° it softens, at 100 to 105° it is transparent, at 107 to 113° it has liquefied. See page 519 for reactions. It is precipitated with difficulty by digitonin but forms a dibenzoate with benzoic acid. Its identity has been questioned.§

(ϵ) **Phytosterin** occurs in all plants; it is similar to cholesterin but is not a single substance. Melts between 132 and 144°. Crystallized in needles with rhombic points. Forms mixed crystals with cholesterin of the shape of phytosterin. $[\alpha]_D = -34.2°$. (See page 399.) Solubility, color reactions and behavior with digitonin are similar to those of cholesterin.

(ζ) **Sitosterin** occurs in the fat of wheat, corn, and rye. Melts at 137.5°. It may be pure phytosterin.

(η) **Stigmasterin** is found in the Calabar bean and in rape oil. Formula $C_{30}H_{48}O$ or $C_{30}H_{50}O$. Melts at 170°. $[\alpha]_D = -45.01°$. Crystallizes like phytosterin and gives similar reactions. It contains 2 double bonds, and therefore forms a tetra-brown acetate, which is difficultly soluble, allowing its separation from phytosterin.

(θ) **Ergosterin** is found in ergot. Melts at 154°. $[\alpha]_D = -114°$ in chloroform. It crystallizes from alcohol in pearly plates.

The amount of sterols occurring in fats has only recently become known. Formerly the total amount of unsaponifiable matter was determined by extraction from the aqueous-alcoholic soap solution with ether, and by crystallization of the ether-extract from alcohol. Exact determination of the amount of sterins became possible with the discovery of the Windaus digitonin method. The digitonin is added in alcohol solution to an alcohol solution of the unknown; the sterol precipitates in combination with the digitonin. The weight of this compound multiplied by 0.2431 gives the amount of sterol (see page 349). The sterin content of natural and hardened fats has been determined|| in this manner.

More direct is the method of Klostermann and Opitz¶ in which by direct precipitation from the fat is obtained the free or uncombined

* Windaus, Ber., **47,** 2487 (1914).

† Windaus, Ber., **49,** 1724 (1916).

‡ Lifschütz, Ber., **41,** 253 (1908); **47,** 1453 (1914).

§ Marcusson, Chem. Ztg., **41,** 577, 590 (1917). Also Chem. Ztg., **42,** 6 (1918).

|| Marcusson and Meyerheim, Z. angewandte Chem., **27,** 201 (1914).

¶ Z. Nahr. u. Genussm., **27,** 713 (1914); **28,** 138 (1914).

sterol, and by precipitation from the fatty acids after saponification of the fat there is obtained the total content of sterol; free sterol but not a fatty acid ester of it will react with digitonin. Table 84 gives the results obtained:

TABLE 84

STEROLS IN ANIMAL AND VEGETABLE FATS

	Material	Total sterol	Free sterol	Combined sterol
Vegetable Fats	Palm oil	0 08	0 06	0.22
	Linseed oil	0 42	0 20	0 22
	Olive oil	0 13	0 09	0.04
	Rape oil	0 35	0 05	0.30
	Poppyseed oil	0.25	0 23	0.02
	Sesame oil	0 55	0.33	0.22
	Peanut oil	0 25	0.19	0 06
	Cottonseed oil	0 31	0 20	0 11
Animal Fats	Lard	0.07 to 0.12	0.07 to 0.12	....
	Butter	0 07	0 07	....
	Beef tallow	0 07	0.07	....
	Mutton tallow	0 03	0 03	....
	Goose fat	0 04	0 04	....
	Oleomargarine	0 11	0 10	0.01
	Cod-liver oil	0 52	0 27	0.25
	Human fat	0.18	0.16	0 02

Sterol esters appear to exist in considerable amount only in vegetable oils and in cod-liver oil; animal fats usually contain only uncombined sterol. Egg yolk may contain as high as 3 per cent of sterol.

(*b*) *Other Unsaponifiable Components*

The unsaponifiable material* left after separation of the sterols may be 45 to 67 per cent of the total unsaponifiable matter in the case of vegetable oils, or 86 to 92 per cent of the total in the case of animal fats. Associated with the laevo-rotatory sterins occur dextro-rotatory unknown alcohols and small amounts of hydrocarbons.

The sterol-free unsaponifiable matter is viscous or salve-like; it has an iodine value of from 56 to 78 (Hübl-Waller). On this depends a method for the detection of mineral oil in linseed oil.† A mineral oil addition lowers the iodine value.

The unsaponifiable matter from the liver oil of two Moroccan fishes contained practically only unsaturated hydrocarbons. Unsaturated hydrocarbons (up to

* Marcusson and Meyerheim, Z. Nahr. u. Genussm., **27**, 713 (1914); **28**, 138 (1914).

† Thoms and Fendler, Chem. Ztg., **28**, 841 (1904).

90 per cent) have been found in Japanese* shark liver oil. In Squalus Mitsukurii was found "squalene" an unsaturated hydrocarbon $C_{30}H_{50}$ with 6 double bonds, a colorless oil of density 0.8587 at 15°.

The unsaponifiable matter of sesame oil has a rotatory power + 52°; on removal of the sterols, its rotatory power, due to sesamin, rises to + 102°. A similar high dextro-rotatory power is shown by mowrah and shea fat.† Mowrah fat contains about 2 per cent of unsaponifiable matter, rotatory power + 27°; of this from 0.26 to 0.44 per cent is insoluble in alcohol and optically inactive, the residue having an optical rotatory power of + 34° and an iodine value of 68.3. It contained 0.04 per cent of phytosterin. Shea fat contained 6.3 to 6.9 per cent of total unsaponifiable, 0.9 to 2.5 per cent of alcohol insoluble inactive material and 0.09 to 0.12 per cent of phytosterin (melts 152 to 153°). The residue had a rotatory power of + 38.5 to + 39.5° and an iodine value of 66.6. These properties may be used for the identification of these fats.

II. Synthesis of Fats

Fats‡ have been synthetically prepared by heating glycerine with calculated amounts of the free fatty acids in sealed tubes to 200 to 260°; mono-, di- and tri-glycerides were formed in this way. The simplest fat, glyceryl triformate, is prepared§ by heating glycerine repeatedly with excess of 100 per cent formic acid. After fractional distillation and recrystallization from liquid ammonia it is obtained in colorless crystals melting at 18° and boiling at 266° (760 mm.), insoluble in cold water and saponified by hot water. Mono- and di-glycerides $C_3H_5(OH)_2OR$ or $C_3H_5(OH)(OR)_2$ are obtained on heating the salts of fatty acids with glycerine mono- or di-chlorhydrin.|| These mono- and di-glycerides resulting from this synthesis are changed to the mixed triglycerides $C_3H_5(OR)(OC_2H_3O)_2$ and $C_3H_5(OR)_2(OC_2H_3O)$ by heating with acetic anhydride. Pure triglycerides are obtained according to Berthelot by heating mono- and di-glycerides with the corresponding acid or, according to Guth, Partheil and Velsen,¶ by heating tribromhydrin with the silver or sodium salts of the fatty acids. A. Grün** obtained diglycerides by heating glyceryl disulphate $C_3H_5(OH)(OSO_3H)_2$ with fatty acids in sulphuric acid solution. A. V. Skopnik†† allowed α-monochlorhydrin to act on the acid chloride of

* Chem. Ztg., **39**, 889 (1915). Seifensiederztg., **43**, 609 (1916). Chem. Soc. Trans. **111**, 56 (1917). Analyst, **42**, 161 (1917). Chem. Umschau, **24**, 118 (1917).

† Z. Nahr. u. Genussm., **27**, 723 (1914); **28**, 73 (1914).

‡ Berthelot, Ann. d. Chim. et de Phys. (3), **41**, 420 (1854).

§ Van Romburgh, Zeit. f. physikal Chem., **70**, 459–461 (II Arrhenius Festband).

|| Krafft, Ber., **36**, 4339 (1903), Guth, Ztschr. f. Biologie, **44**, N. 26, I, 78.

¶ Archiv. d. Pharmacie, **238**, 267 (1900).

** Ber., **38**, 2284 (1905).

†† Dissertation, Zurich, 1909.

lauric acid, obtaining in this way α-lauro-α'-chlorhydrin; this product with potassium myristate formed α-lauro-α'-myristin, which by reaction with stearyl acid chloride produced the triglyceride α-lauro-β-stearo-α'-myristin. Mixed glycerides can also be obtained by the action of mono- and di-glycerides on fatty acids, for example oleo-distearin by heating α-distearin with oleic acid.* The heating of acid anhydrides and acid chlorides or of fatty acid esters of α-monochlorhydrin with the potassium or silver salts also leads to the formation of mixed glycerides.†

Optically active butyrins have been prepared by Abderhalden and Eichwald.‡ Lauro-, stearo-and oleo-dibutyrin were slightly laevo-rotatory. Up to the present time optically active mixed glycerides have not been identified in nature, probably because they have a great tendency to reversal and therefore tend to assume an optically inactive condition.

A commercially feasible fat synthesis has not yet been discovered. Lindner has however described a biological synthesis of fat from sugar (page 370). A synthesis from paraffins and ethylenes has been attempted (page 371).

III. Transformation of the Components of Fats

By the action of nitrous acid liquid oleic acid is transformed into the isomeric elaidic acid of melting point 51°, while ricinoleic acid is similarly transformed into ricinelaidic acid of melting point 53°. Triolein and ricinolein undergo similar stereoisomeric changes.§

$$\begin{array}{ll} CH_3\cdot(CH_2)_7\cdot CH & \\ \qquad\qquad\qquad \Vert & \\ \qquad\qquad\qquad CH\cdot(CH_2)_7\cdot COOH & \\ \qquad\qquad\qquad \text{normal oleic acid} \end{array} \qquad \begin{array}{r} CH_3\cdot(CH_2)_7\cdot CH \\ \Vert \\ HOOC\cdot(CH_2)_7\cdot CH \\ \text{elaidic acid} \end{array}$$

On this property depends the test for olive oil and other non-drying oils containing considerable amounts of olein, as developed principally by Finkener. Drying oils (as oils containing much linoleic acid) remain liquid; the non-drying oils, containing principally triolein, become solid in the presence of nitrous acid.

Brassidic acid has the same relation to erucic acid as has elaidic acid to oleic acid.

* Kreis and Hafner, Ber., **36,** 2766 (1903).

† Grün and Schacht, Ber., **40,** 1778 (1907). Grün and Theimer, Ber., **40,** 1792 (1907). Also Z. angewandte Chem., **29,** 37, 46 (1916).

‡ Berichte, **48,** 1847 (1915).

§ Baruch, Ber., **27,** 173 (1893).

According to Mascarelli and Sanna* the isomeric brassidic and iso-erucic, and behenic acids form mixed crystals, but erucic acid does not form mixed crystals with these acids. Brassidic and iso-erucic acids must have a similar structure.

The determination of the position of the double bond in oleic acid is made by splitting the chain at this point. A general formula for oleic acid is $CH_3 \cdot (CH_2)_n \cdot CH : CH \cdot (CH_2)_{14-n} \cdot COOH$. The acid is brominated with the formation of dibromstearic acid:

$CH_3 \cdot (CH_2)_n \cdot CHBr \cdot CHBr \cdot (CH_2)_{14-n} \cdot COOH$. On treatment with caustic potash under pressure, 2 molecules of HBr are split off, stearolic acid forming: $CH_3(CH_2)_n \cdot C \equiv C \cdot (CH_2)_{14-n} \cdot COOH$. On treatment with concentrated sulphuric acid, this changes to ketostearic acid: $CH_3 \cdot (CH_2)_n \cdot CO \cdot (CH_2)_{16-n} \cdot COOH$. This on treatment with hydroxylamine produces two oximes; which undergo the Beckmann rearrangement on treatment with concentrated sulphuric acid, two substances forming:

I. $CH_3 \cdot (CH_2)_n \cdot NH \cdot CO \cdot (CH_2)_{15-n} \cdot COOH$

II. $CH_3 \cdot (CH_2)_n \cdot CO \cdot NH \cdot (CH_2)_{15-n} \cdot COOH$

On treatment of the mixture with hydrochloric acid at 180 to 200°, a decomposition of the molecule takes place at the point of the original double linking and there is obtained from I, a normal amine $CH_3 \cdot (CH_2)_n \cdot NH_2$ and a dibasic acid $COOH \cdot (CH_2)_{15-n} \cdot COOH$; from II is obtained a monobasic acid, $CH_3 - (CH_2)_n \cdot COOH$ and a amino-acid $NH_2 \cdot (CH_2)_{15-n} \cdot COOH$.

Fahrion† has described the possible isomers of oleic acid, and those actually prepared. In the seed of parsley is found 6.7 oleic acid $CH_3 \cdot (CH_2)_{10}\ CH = CH \cdot (CH_2)_4 \cdot COOH$; *9, 10 oleic acid is the usual* constituent of fats and oils of animal and vegetable origin; while 10, 11 oleic acid $CH_3 \cdot (CH_2)_6 \cdot CH = CH \cdot (CH_2)_8 \cdot COOH$ is obtained on distilling candle-stock fatty acids.

Molinari and Soncini‡ state that one mol of oleic acid absorbs three atoms of oxygen (one mol of ozone); the addition product $C_{18}H_{34}O_5$, on heating, passes almost quantitatively into one mol of *n*-caprylic acid and a keto-acid $C_{10}H_8O_3$; the double bond must therefore be assumed as present near the middle of the chain. A confirmation of this is found in the decomposition of oleic acid into pelargonic acid $C_8H_{17}COOH$ and azelaic acid

$$COOH \cdot (CH_2)_7 \cdot COOH$$

on careful oxidation. Linoleic acid absorbs two mols of ozone.

Harries and Thieme,§ however, found that oleic acid on treatment

* Chem. Zentralblatt, **1916,** I, 55.
† Chem. Umschau, **23,** 2 (1916).
‡ Chem Ztg. **29,** 715 (1905).
§ Ber., **38,** 1630 (1905); **39,** 3728 (1906).

with ozone absorbed four atoms of oxygen, forming the ozonide which reacts with two molecules of water to form 1 mol of *n*-nonyl aldehyde

$$\begin{array}{l}
CH_3 \cdot (CH_2)_7 \cdot CH \cdot CH \cdot (CH_2)_7 \cdot C \cdot OH \\
\qquad\qquad\quad\;\; | \qquad\; | \qquad\qquad\qquad\;\; \| \\
\qquad\qquad\quad\;\; O - O \qquad\qquad\quad\;\; O \\
\qquad\qquad\quad\;\; \diagdown\!\diagdown \;\; \diagup\!\diagup \qquad\qquad\quad\; \| \\
\qquad\qquad\qquad\;\; O \qquad\qquad\qquad\;\;\; O
\end{array}$$

and a mol of the half-aldehyde of azelaic acid, hydrogen peroxide forming at the same time. From the ozonide with four atoms of oxygen (which they call oleic acid ozonide peroxide), they obtained, by washing with water and sodium bicarbonate and drying with ether the isolated product, a substance of the same formula as the ozonide obtained by Molinari and Soncini.

The oxidation products obtained* by the action of alkaline potassium permanganate (page 375) serve to identify these acids. By treating oleic and erucic acids with hypochlorous acid and caustic potash or with persulphate, Albitzky† obtained dioxy-acids melting at 99.5° and 100° which are also formed by oxidation of elaidic and brassidic acids in alkaline permanganate solutions; by oxidizing these latter acids in acid solution, there were formed dioxy-acids melting at 136.5° and 132°, which are obtained by the oxidation of oleic and erucic acids in alkaline solution.

In approximately neutral or faintly alkaline solution, Holde and Marcusson‡ prepared keto-oxystearic acid

$$CH_3 \cdot (CH_2)_7 \cdot CO \cdot CH\,(OH) \cdot (CH_2)_7 \cdot COOH$$

from oleic acid and this substance passes into stearoxylic acid $CH_3 \cdot (CH_2)_7 \cdot CO \cdot CO \cdot (CH_2)_7 \cdot COOH$ on oxidation with acetic and chromic acids.

The normal structure of stearic acid was proven by Krafft by gradual decomposition into acids of low molecular weight.

On fusion of oleic acid with alkali§ a good yield of acetic and palmitic acids was obtained; it has been shown however that all normal unsaturated acids split between the alpha and beta carbon atoms irrespective of the position of the double bonds. The fusion method gives no information about the position of the double bond. Wagner‖ in attempting to explain the decomposition into two simpler acids during fusion assumed the intermediate formation of a dioxy-acid, and then a change

* Saytzeff, J. f. prakt. Chem. (2), **34**, 304, 315.
† J. f. prakt. Chem., **61**, 65; Ber., **33**, 2909 (1900).
‡ Ber., **36**, 2657 (1903).
§ Marane, Ber., **2**, 359 (1869).
‖ Ber., **21**, 3353 (1888)

into a keto-acid. Eckert *tested the assumption by* fusing* the presumed intermediate products *with alkali but in no case obtained the same products.* Dioxystearic *on alkaline fusion* produced *pelargonic acid* $CH_3 \cdot (CH_2)_7 \cdot COOH$ and azelaic acid $COOH \cdot (CH_2)_7 \cdot COOH$. Dioxybehenic acid gave pelargonic acid and *brassylic acid. From sativic acid were obtained acetic acid, caproic acid and azelaic acid, indicating the following formula for sativic acid:* —

$$CH_3 \cdot (CH_2)_4 \cdot CHOH \cdot CHOH \cdot CH_2 \cdot CHOH \cdot CHOH \cdot (CH_2)_7 \cdot COOH.$$

Linolic acid therefore has the formula:

$$CH_3 \cdot (CH_2)_4 \cdot CH = CH \cdot CH_2 \cdot CH = CH \cdot (CH_2)_7 \cdot COOH$$

From linusic acid by potash fusion was obtained acetic acid, propionic acid and azelaic acid, confirming the formula suggested by Erdmann† for linolenic acid: —

$$CH_3 \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CH : CH \cdot (CH_2)_7 \cdot COOH$$

Beta-ketostearic acid could not be prepared Eckert from his own and other‡ experiments concludes that the intermediate compounds suggested by Wagner did not form on alkaline fusion. He concluded that there was a shift of the double bonds of oleic to the end of the chain.

When sulphuric acid acts on oleic acid, elaidic acid, and iso-oleic acid sulphuric acid esters of oxystearic acids are obtained which on hydrolysis produce free oxystearic acids; in the same way, erucic acid, prepared from rape oil, § yields oxybehenic acid.

Regarding the constitution of elaeostearic acid see page 360.

It has been shown|| that lignoceric acid $C_{24}H_{48}O_2$ does not contain a straight carbon chain; it is an isomer of normal tetracosanic acid.

Ricinoleic¶ acid has the formula: —

$$CH_3 - (CH_2)_5 \cdot CHOH \cdot CH_2 \cdot CH : CH(CH_2)_7 \cdot COOH$$

Clupanodonic acid was formerly considered to be the normal acid of the series $C_nH_{2n-8}O_2$. The octabromide has however been reduced with zinc dust and alcohol, again brominated and the acid thus produced reduced by colloidal palladium and alcohol, and the product tested for purity. Besides stearic acid, there was obtained a low melting mixture of saturated acids, thus leading to the conclusion that clupanodonic acid is a mixture of isomeric acids containing four double-bonded linkings; some of these contain forked carbon chains.

IV. Spontaneous Changes in Fats and Oils

(a) *Rancidity*

The fats under certain conditions become rancid, which is concomitant with a change into free fatty acids and decomposition products of the glycerine. The peculiar odor and rancid taste of a rancid

* Monatshefte, **38**, 1 (1917).

† Ber., **42**, 1334 (1909).

‡ Chem. Zentral bl **1915**, I, 934.

§ Grün and Fanko, Chem. Umschau, 23, **15**, 33 (1916).

|| Monatshefte, **34**, 113 (1913). J. Biolog. Chem., **18**, 477 (1914).

¶ Ber., **27**, 3121 (1894).

fat are easily recognized in the case of an edible fat like butter, which contains glycerides of the more volatile acids; but in industrial products not containing volatile acids it is much harder to detect. Free glycerine seems not to be present; it appears to be decomposed immediately on formation; for this reason oils containing much free acid, for example rancid olive oil, never show a separation of glycerine (which is insoluble in oils). The tendency to separate free fatty acids is quite pronounced in the case of palm fat, which often consists only of free fatty acids. These changes are probably in part due to the action of enzymes since it has been shown* that every fatty oil is split by the action of the lipase in the seeds of the castor oil plant; it is assumed therefore that the rapid decomposition of the fats is brought about by some enzyme.

A. Schmidt† claims that aldehydes and ketones are present in rancid oil, as may be shown by distilling with steam and testing the distillate with the hydrochloride of phenylene diamine. According to Jorissen,‡ when butter, cod-liver oil and olive oil are exposed to light, hydrogen peroxide is formed. Fish oils when exposed to light lose their characteristic tendency to react with nitric acid of specific gravity 1.50. Dietz § found that rancid fats contain peroxides which with potassium iodide and starch solutions gave a violet or blue color. According to Amthor || and Reimann¶ the rancidity of fats is due to the action of enzymes and microörganisms, the rancid odor of butter being due principally to esters of acids of low molecular weight and to traces of free, volatile acids. Amthor supposes that the microörganisms change the milk sugar of the butter into alcohol which unites with the acids to form esters.

Rancid fat has higher acetyl values than fat which is not rancid; this may be explained (without assuming the occurrence of mono- and di-glycerides, the presence of which is not proven) by the presence of oxyacids, anhydrides, lactones and volatile acids (Marcusson).

It has been claimed** that oxygen is not necessary to produce rancidity, that the action of light alone is sufficient, as fats will bleach and produce the odor and taste typical of rancidity, in the absence of air.

* Connstein, Hoyer and Wartenberg, Ber., **35**, 3988 (1902).

† Zeit. f. anal. Chem., **37**, 301 (1898).

‡ Chem. Ztg., **22**, 162 (1898).

§ Chem. Ztg., **29**, 705 (1905).

|| Zeit. f. anal. Chem., **38**, 10 (1899).

¶ Zentralb. f. Bacteriol., **6**, Nr. 5–7 (1900).

** Wagner, Walker and Ostermann, Z. Nahr. u. Genussm., **25**, 704 (1913).

On the other hand, oxygen is said* to be absolutely necessary as the rancid fats always contain peroxide which can be shown to be present with the aid of the haemoglobin-guaiac reaction.

Ten grams of oil or fat are shaken for one minute with 4 to 5 drops of blood (or haemoglobin solution), 10 drops of tincture of guaiac, and 10 c.c. of water. Rancidity is shown by the blue color, which is accentuated by adding 95 per cent alcohol. Rancid fats heated to above 200° no longer give the reaction.

Oleic acid, the chief component of liquid and non-drying fats, changes considerably under the action of air. Salkowski found in a sample of oleic acid kept for years, † a crystalline acid melting at 48°. Senkowsky‡ assumed this to contain (on the basis of the ester and iodine values, etc., without isolating these substances) stearolactone, oxystearic acid and only 31 per cent of oleic acid. Fahrion § attributed the decrease of the iodine value to polymerization, without having separated chemically defined bodies.

(b) *Drying of Oils*

The drying process, in its details, is no more clearly understood than is the rancidity of fats. Common to both processes there is an increase in the amount of oxy-acids (shown by an increase in the ester value); a polymerization takes place which (as does the oxidation of the unsaturated bodies) causes an increase in specific gravity and viscosity. The oxidation and polymerization in the drying process take place, not only with the compounds with one double bond, but also with those glycerides and acids containing two double bonds (linoleic, linolenic, etc., acids), the changes of the latter bodies giving rise to the oxidized, polymerized and partially dehydrated substances, more or less hard, insoluble in ether and naphtha, only soluble in alcoholic solutions of alkali.

The insoluble oxidized product called linoxyn can however be dissolved|| in benzol after long digestion. On oxidizing linseed oil (or the acids from linseed oil) at 100°, Salway¶ found that acrolein was formed: this, on shaking with silver oxide, produced the silver salt of acrylic acid. Oleic acid under the same conditions produced

* Vintilesco and Popesco, J. Pharm. Chem., **12**, 318 (1915).

† Festschrift zum Virchow-Jubiläum, **1890**, 19.

‡ Zeit. f. physiolog. Chem., **1898**, 434.

§ Chem. Ztg., **17**, 434 (1893); **23**, 770 (1899).

|| Fritz, Chem. Umschau, **23**, 29 (1916).

¶ J. Chem. Soc., **109**, 138 (1916).

no acrolein. From linolenic acid was formed a di-peroxide: —

$$\begin{array}{lllllllll} CH_3 - (CH_2)_5 \cdot & CH & \cdot & CH & \cdot CH = CH \cdot & CH & \cdot & CH & \cdot (CH_2)_5 \cdot COOH \\ & | & & | & & | & & | & \\ & O & - & O & & O & - & O & \end{array}$$

This gave fumaric aldehyde on decomposition; on further decomposition acrolein, CO and CO_2 were produced.

In the drying of oils both oxidation and polymerization take place. The drying may be increased by adding dryers (such as manganese resinate or linoleate) which act at ordinary temperatures or by boiling with manganese borate. These produce metallic soaps (salts of the unsaturated acids) which may act catalytically. The actual reasons for the oxidation and polymerization are still in dispute.*

Recent experiments of Olsen and Ratner† have shown that linseed oil in drying liberates water and carbon dioxide and absorbs oxygen; for example one sample in 74 days lost 1.87 per cent of carbon and 14.7 of hydrogen while it absorbed 37.8 per cent of oxygen. Orlow‡ found an absorption of 15 to 16 per cent of oxygen, solidification taking place when 12 per cent had been absorbed; this corresponded to the amount of oxygen equivalent to the iodine value of the oil.

It is claimed§ that the humidity of the air affects the oxidation process. It has also been stated that the drying process is accelerated by the presence of free acids and repressed by alkali and alkali soaps. This has been flatly contradicted; boiled linseed oil stirred with lime (from marble) dried more rapidly than oil alone. Pure linseed oil stirred at 50° with slacked lime was changed into solid linoxyn which contained 38.7 per cent of oxy-acids insoluble in petroleum-ether.

Tung (wood) oil has the property of absorbing oxygen, the oxidation being accompanied by solidification;|| polymerization, due to molecular rearrangements, may also take place in the absence of air. The former process takes place under the influence of light at room temperature and leads to a crystalline body, soluble in solvents for fats, and having a melting point of 32°; the polymerization takes place at higher temperatures (150°) and gives products which are not soluble in fat solvents and which do not melt. The mechanism of oxidation of tung oil is much the same as that of linseed oil; the assumption that tung oil drys outward from the interior

* Z. angewandte Chem., **28**, 249 (1915).
† Chem. Ztg., **36**, 1188 (1912).
‡ Chem. Zentrallblatt, **1912**, I, 861.
§ Chem. Umschau, **22**, 19, 60 (1915).
|| Fahrion, Farbenztg., **17**, 2530, 2583, 2635, 2689 (1912).

is incorrect. Wood oil dries more rapidly at ordinary temperatures than does linseed oil, at higher temperatures much more rapidly. Polymerization is not reversed by saponification; this therefore gives a means for distinguishing between oxidized and polymerized oils: the acids of polymerized oils are soluble in petroleum ether, those of oxidized oils are insoluble. Polymerization of wood oil acids is quite different from that of the oil itself, liquid products being formed.

The polymerization of the Chinese wood oil, its transformations under the influence of light, and its increase in refractive power are said * to depend on the structure of elaeostearic acid; this is an isomer of linoleic acid, differing from it in the location of the double bonds, as was shown by reduction to stearic acid. On standing one year in a vessel free from air 6 per cent of wood oil changed into a crystalline body,— elaeosterin, of melting point 61 to 62°.

The polymerization of linseed oil is accelerated by oxidation, but to a lesser degree than is tung oil; thickening and gelatinization may moreover take place in a vacuum and in indifferent gases. The actual changes taking place are as yet unexplained,† though much disputed.

Krumbhaar boiled linseed oil and tung oil in large kettles in the absence of air (in a stream of carbon dioxide).

After heating for 20 hours to 300° linseed oil was only slightly stringy, wood oil gelatinized at from 200 to 260°. At 300° it solidified so quickly that samples could not be withdrawn, and the temperature rose, as a result of the solidification, to 320°, an exothermic change taking place. The larger the quantity of oil the more intense the exothermal effects; these may lead to the much-feared wood-oil fires. Wood oil thickens, with the same amount of heating, much more rapidly than does linseed oil, the acid value not changing appreciably during the duration of the heating. Linseed oil thickens very slowly at 200°, more rapidly at 260°, quite considerably at 300°, without gelatinizing. Wood oil gelatinizes at 200° in 4 hours, at 260° in 20 minutes, and in a few minutes at 300°.

The refractive index of linseed oil is 1.479 at 25° but rises to 1.496 at 300°; that of wood oil drops from 1.515 to 1.446 after 4 hours at 200°. The increase with linseed oil may be due to the formation of free acid which has a higher refractive index.

* Fakin, J. russ. phys.-chem. Ges., **45**, 283. Majuna, Ber., **45**, 1561 (1912). Morell, J. Chem. Soc., **101**, 2082 (1912).

† Kronstein, Ber., **49**, 722 (1916). Fahrion, Farbenztg., **17**, 2418, 2530 (1910). Wolff, ibid., **18**, 1171 (1911). Krumbhaar, Chem. Ztg., **40**, 937 (1916).

V. Physiology of the Fats

On the basis of feeding experiments it is now assumed that the fats may form in the animal body from carbohydrates while protein material does not give rise to the formation of fat directly. It is also accepted that fat is formed from its components in the animal organism. Hanriot* and Kastle and Loevenhart† have shown that the synthesis of fats under the influences of enzymes on glycerine and fatty acids is possible outside the body. Loevenhart‡ assumes that the synthesis in the body is caused by lipases. Others§ have shown that fats are synthesized in the body from glycerine and fatty acids, and feeding experiments with animals have shown|| that erucic acid (not normally present in the animal body) in the food leads to the formation of erucin which can be detected in the body.

It has also been shown that ethyl esters of the acids of tallow are 96 per cent absorbed by dogs, and 98 to 99 per cent absorbed when mixed with 40 per cent of beef tallow. Mixtures of beef tallow with 30 per cent of such ethyl esters were assimilated by human beings to the extent of 93 to 95 per cent.

There is some disagreement as to how the fat is absorbed in the body but the consensus of opinion seems to be that it is first hydrolyzed and then absorbed.¶ The higher-melting fats are probably less digestible** than the lower-melting ones.

The pancreatic juice contains an enzyme, steapsin, which hydrolyzes the fats; the 0.2 to 0.4 per cent of sodium carbonate in the juice neutralizes free acids, the soaps formed aiding in the production of an emulsion in the alkaline medium. The fats (including lecithins) are digested into fatty acids and glycerine which are then absorbed by the intestinal walls. The bile-acid salts aid in the production of the fat-emulsion, and in moistening the cell-walls of the intestines, and thus

* Schacht, Inaugural Dissertation "Beitrage zur Synthese der Fette. Symmetrische Glyceride," Zurich, gives literature.

† Amer. Chem. Jour., **24,** 491 (1900). See also Doyen and Morell, Compt. Rend., **134,** 1254.

‡ Amer. Jour. Physiol., **6,** 331.

§ Rosenfeld, Allgem. Med. Zentralbla., **1901,** Nr. 73; Munk, DuBois Reymond Archiv, **1883,** 273; Virchows, Archiv, **95,** 407; Lebedeff, Med. Zentralblatt, **1882,** Nr. 8.

|| Jahrbuch f. Thierchemie, **16,** 42.

¶ Pflüger, Pflüger Archiv., **82,** 303; see however, Munck, Chem. Zentralblatt, 1900, II, 390, also Henriques and Hansen, Zentralbl. f. Physiolog., **14,** 313. Bokorny, Chem. Ztg., **35,** 630 (1911).

** Chem. Ztg., **24,** 647 (1900). Zuntz, Nahrung und Ernahrung, 1918.

help in the absorption. In the cell the fat is resynthesized, probably by cell-lipases. The fat is stored in the body as reserve food material. When required it is used by the body for muscular effort, being burned to carbon dioxide and water. If large amounts of fat are eaten, a part will pass into the feces; for this reason attempts have been made to recover such fats from sewage (page 370).

The butter-like, yellow human fat has a density of 0.918, melting point 17.5°; it contains 4.9 to 6.9 per cent of stearic acid, 16.9 to 21.1 per cent of palmitic acid, and 65.8 to 86.7 per cent of oleic acid, combined as tripalmatin and oleo-distearin. About 0.33 per cent of unsaponifiable matter and 0.084 per cent of lecithin are contained. Adipocere is formed from fat, and contains free fatty acids (acid value 203), with 16.7 per cent of unsaponifiable matter.

Human hair contains according to different observers from 2.6 to 14 per cent of fat; the amount may depend upon the amount of hair-oil used. Hair-fat has a saponification value of 113.9 to 139.4, while the unsaponifiable matter is about 44 per cent. It is said to resemble wool-fat; it contains esters of cholesterin and other alcohols.

The high fat (and wax) content of some microörganisms (page 370) such as bacteria (diphtheria, syphilis) is of interest biologically and therapeutically. The tubercle bacillus is especially rich in wax which is the carrier of the color reactions given by anilin dyes on staining. Robert Koch called attention to the fat content of the tubercle bacillus and considered this the cause of their resistance to acids. The mononuclear lymphocytes of the blood contain a fat-splitting ferment which can act hydrolytically on the wax of tubercle bacilli; these cells, which are found in the lymph sacs, in the spleen, and elsewhere, are considered by some as a specific defense against the tubercle bacilli. Wassermann states that a living body forms more fat- and wax-splitting (that is tubercle bacilli-destroying) enzymes, the greater the amount of fat consumed in the form of cod-liver oil, butter, milk, etc.

The cause of the turgidity* of many plant and animal tissues rich in fat is the formation of a fat-emulsion. An emulsion of two liquids has a much greater viscosity than either of the components. The materials emulsifying the oil are proteins, soaps, and carbohydrates, namely, the constituents of protoplasm. By destroying the emulsion, a pathological softening of the tissue results, and the viscosity of the components is decreased.

Through the poisonings resulting from the use of margarine (in

* Fischer and Hooker. Kolloid Ztschr., 18, 242 (1916).

Germany in 1910) to which had been added Indian maratti oil* (chaulmugra fat), the first example of a poisonous fat was discovered. All other pure fats, neglecting the purgative action of castor oil, are not poisonous. However soaps (for example sodium oleate) are said to affect the heart action; injected intravenously they decrease the blood pressure and act as narcotics (Munck). Free fatty acids (from butyric acid upwards in molecular weight), in so far as they are soluble in water, and aldehydes, are poisonous.

VI. Theory of Saponification

The fats (and waxes) are converted into soaps and glycerine (and higher alcohols) on boiling with aqueous alkalies. The end reaction is given by the following equation in which R represents an acid radical (for example $C_{16}H_{31}O$, the palmitic acid residue):

$$C_3H_5(OR)_3 + 3\,NaOH \rightarrow C_3H_5(OH)_3 + 3\,NaOR.$$

According to indirect physico-chemical experiments of Geitel† and of Kremann,‡ the saponification process is supposed to take place by steps, that is, with the intermediate formation of di- and mono-glycerides. This had previously been assumed to be the case by Alder Wright.§ Geitel also assumed the presence of mono- and di-glycerides in rancid fats formed by a partial hydrolysis of the fat by water. The discovery of dierucin in rape oil|| is a confirmation of this; Strohmann and Kerl¶ stated that the dierucin is found only in oil refined with sulphuric acid but Reimer** has shown that dierucin is found in the raw oil.

According to experiments of Fantos†† the saponification of pure glycerides by aqueous alkali is a quadrimolecular reaction and takes place by the reaction of 3 mols of KOH and 1 mol of triglyceride according to the theory of Balbiano.‡‡ Kellner§§ states that, with aqueous alkali in an open vessel, the reaction is quadrimolecular but that in an autoclave, mono- and di-glycerides form. Although the physico-chemical experiments of Kremann tend to show that the reaction takes

* Thoms and Mueller, Z. Nahr. u. Genuss., **22,** 226 (1911). Chem. Ztg., **35,** 630 (1911).

† J. f. prakt. Chem., 1897, **55,** 417; **1898,** 113.

‡ Monats. f. Chem., **1906,** 607.

§ Animal and Vegetable Fats and Waxes, London, 1894.

|| Reimer and Will, Ber., **19,** 3320 (1886).

¶ Muspratt, 1891 (3), 650.

** Ber., **40,** 256 (1907).

†† Monatsschr. f. Chem., **25,** 919.

‡‡ Ber., **36,** 1571 (1903).

§§ Chem. Ztg., **33,** 453 (1909).

place in steps, he assumes that the rate of saponification is so great that the isolation of the intermediate products is not possible; this would explain the negative results of Balbiano and of Marcusson* in the saponification of tribenzoin and fats with aqueous alkali. The latter has however shown, in confirmation of Kellner, that, in saponifying in an autoclave, the formation of lower glycerides can be directly demonstrated,† because they are not directly further saponified by alkali but remain in part dissolved in the undecomposed fat.

Grün and Corelli‡ showed that in the saponification of fats with sulphuric acid, the process takes place in steps, but they isolated only diglycerides together with unchanged triglycerides, because the monoglycerides were too quickly transformed to be isolated.

Bouis§ and later Kossel and Obermüller|| showed that the fats saponify very rapidly in ether solution under the influence of sodium alcoholate, the ethyl esters of the fatty acids being formed as intermediate products. By the further action of water, which cannot be absolutely excluded, glycerine and sodium hydroxide are formed, the

$$C_3H_5(OR)_3 + 3\,C_2H_5ONa \rightarrow C_3H_5(ONa)_3 + 3\,ROC_2H_5.$$

latter then saponifying the ethyl esters.

$$3\,C_3H_5(ONa)_3 + 3\,H_2O \rightarrow 3\,C_3H_5(OH)_3 + 3\,NaOH.$$

According to Bull,¶ sodium alcoholate, in the absence of water, cannot saponify glyceride fats; not only is the saponification facilitated by the presence of water but the solubility of the salts in ether also.

According to Henriques** the fats and most of the waxes, after 10 to 12 hours treatment with alcoholic potash in petroleum ether solution at room temperature, are completely saponified, whereby the following intermediate products form in the saponification of, for example, triolein,

$$\begin{aligned} &C_3H_5(C_{18}H_{33}O_2)_3 + 3\,NaOH + 3\,C_2H_5OH \\ &\qquad \rightarrow C_3H_5(OH)_3 + 3\,C_{18}H_{33}O_2 \cdot C_2H_5 + 3\,NaOH \\ &\qquad \rightarrow C_3H_5(OH)_3 + 3\,C_{18}H_{33}O_2Na + 3\,C_2H_5OH \end{aligned}$$

The ethyl esters of the fatty acids can be isolated by taking one-third of the theoretical amount of alkali necessary for saponification and then, after allowing to stand for one day, separating the esters from the saponified fat by the method of Spitz and Hönig (page 197).

* Ber., **39,** 3466 (1906); **40,** 2905 (1907).

† Zeit. f. angew. Chem., **26,** 173 (1913).

‡ Zeit. f. angew. Chem., **25,** 665, 947 (1912).

§ Compt. rend., **45,** 35.

|| Zeit. f. physiolog. Chem., **15,** 321, 330 (1891).

¶ Chem. Ztg., **24,** 814, 845 (1900).

** Chem. Ztg., **10,** 697 (1898).

Saponification must be distinguished from hydrolysis; the latter can be brought about by the action of mineral acids, by superheated steam or by enzymes (see also page 440).

The fats can be split* by heating the glycerides with absolute alcohol (best methyl alcohol) containing 1 to 2 per cent of hydrochloric acid.

$$C_3H_5(COOR)_3 + 3\,R'OH \rightarrow C_3H_5(OH)_3 + 3\,RCOOR'.$$

The methyl esters of the fatty acids form, the alcoholysis being facilitated by using a neutral solvent like naphtha or carbon tetrachloride. By the alcoholysis of cocoanut fat the methyl esters of caprylic, of capric, of lauric and of myristic acids, etc., were obtained after fractionation. Trilaurin and trimyristin predominate in cocoanut fat. The method can also be used for the scientific analysis of fats.

By treatment of tri-stearin with alcoholic sulphuric acid Grün† obtained the ethyl ester of stearic acid, and mono- and distearin. Alcoholysis also proceeds in stages.

VII. Extraction and Treatment of Fats

The vegetable oils occur principally in the seeds, from which the oil is extracted by hydraulic pressure or by means of naphtha, carbon disulphide, chlorinated hydrocarbons, etc.; the animal oils are obtained by melting out the fat from the fat-containing tissues with or without steam, or by extraction with naphtha or other solvents.

For extraction of fats by solvents, carbon disulphide, naphtha, carbon tetrachloride and trichlorethylene are used industrially. The last two are not combustible; trichlorethylene attacks metals less than does carbon tetrachloride. These chlorinated bodies have a specific gravity decidedly higher than naphtha, thus making the weight of a given volume of solvent greater, and for a given volume a greater weight must be used. On the other hand the heat of vaporization and the heat capacity of the chlorinated bodies is less. The extracted oils are in many cases less pure and more solid in consistency than those melted out or pressed out because the solvents easily dissolve coloring matter and solid resinous bodies; for example, bone fat extracted with naphtha, because of higher content of solid glycerides, potassium soaps and impurities, is generally darker in color than when obtained from bones and hoofs by simple steaming. Edible oils may also be obtained by extraction with solvents.

Many oils are used both raw, after settling, and refined, as for ex-

* Haller, Compt. rend., **143**, 657, 803 (1906).

† Chem. Umschau, **24**, 15 (1917).

ample linseed. Other oils, especially rapeseed oils, must first be freed from coloring matter and other non-fatty material which may be dissolved or suspended in the oil (resin, mucilaginous material, odorous substances, etc.). In many cases this may be done by treatment with fuller's earth, or with concentrated sulphuric acid, running off the clarified oil and then washing free from acid.

TABLE 85

	Boiling point °C.	Specific heat capacity at 18°	Latent heat of vaporization
Carbon disulphide	46 5	0.24	85.
Naphtha	60 to 100	0 401	92.3
Carbon tetrachloride	76 5	0 131	46 6
Trichlorethylene (density 1.47)	88 0		.....
Benzol	80 3	0.41	94.

When the oil contains free fatty acids and is to be used as a lubricant, or for edible purposes, the acidity must be removed; this is accomplished by treatment with alkaline materials, which are later removed by washing with water, or if insoluble like magnesia, by settling and filtration.

Cotton oil is clarified by treatment with alkali, the soap formed eliminating the coloring matter; final clarification is brought about by filtration through fuller's earth.

In the refining of fatty oils with sulphuric acid, an excess of acid, or too long continued treatment, or too high a temperature may change considerable quantities of the oil into fatty acid, or acid sulphur derivatives, and glycerine. Even if the subsequent washing with water will again change the sulphur derivative into free sulphuric acid and free fatty acid, and the mineral acid is removed, there will always remain a considerable amount of free fatty acid; this is shown by the frequent greater acidity of the refined oils as compared with the unrefined materials which always contain free acid. Carefully purified oils contain no free acid, or much less than the crude raw oils. Crude rape oils rarely contain less than 0.7 per cent or more than 1.5 per cent of free acid (calculated as oleic acid); with oils which are not carefully refined, the acidity may rise to 6 per cent. With crude neat's foot oil it may be as high as 28 per cent (calculated as oleic acid).

Zinc chloride solution, potassium or sodium hydroxide, or ammonium hydroxide solution are used for purification of fats; these bodies do not

produce free fatty acids. Baskerville* recommended that a neutral organic substance (like cellulose) be heated with caustic soda and the oil, the mixture then treated with calcined soda or sodium sulphate to remove water, and the oil then filtered. This is said to give from 1 to 10 per cent more oil than the older methods.

Odorous substances, in so far as these are derived from volatile acids from rancid oils, can be removed with soda solutions or by steam. With fish oils the latter fails, so that the best way at present available for removing their odor is hydrogenation. According to Tsujimoto† the main cause of the bad odor of fish oils is clupanodonic acid (and its homologues of the series $C_nH_{2n-8}O_2$); amines from proteins also contribute to the odor. If the fatty acids of the fish oils or their esters are distilled in a vacuum, the unsaturated acids remain in the residue and the distillate is much less odorous; oils thus prepared were for a long time considered by analysts to be a mixture of horse fat and neat's foot oil.

Oils are bleached by oxidizing action (potassium bichromate and sulphuric acid, bichromate and hydrochloric acid, hydrogen peroxide, potassium permanganate and sulphuric acid, etc.), or by simple exposure to air and sunlight (with bone oils), or by treatment with animal charcoal, or fuller's earth. Recently perborates, percarbonates and organic peroxides (benzoyl peroxide) have been used for bleaching. Fuller's earth is used for bleaching tallow, bone oils, cottonseed oil, etc. In some cases sulphurous acid or sodium bisulphite has been used, the coloring matter being destroyed by reduction.

Table 86 gives details regarding the manufacture of some vegetable oils, important industrially.

Vegetable and animal fats are used as edible oils (olive, peanut oil, butter, etc.); certain animal fats are used as lubricants or in currying leather (fish oils); drying oils are used for paints and artists' colors, for putty, linoleum, etc. (linseed, sunflower, poppy-seed, soja bean, perilla and Chinese tung oil are used). Non-drying oils are used for lubrication; for example castor oil is used in airplane motor lubrication, as it has a high viscosity and is insoluble in gasoline with which it is sprayed into the cylinders. Blown rape oils are also used for lubrication (in marine oils, when mixed with mineral oil). Fish oils under the action of a silent electric discharge, are changed to oils of a higher viscosity. Semi-drying oils (cotton, sesame) are used in the manufacture of oleomargarine.

* Chem. Ztg., **42,** 222 (1918).

† Chem. Rev., **20,** 8 (1913). D. R. P. 294778, and 271060.

TABLE 86
Vegetable Fatty Oils

Kind of oil	Olive oil	Rape oil (Colza oil)	Mustard oil (black and white mustard oil)	Castor oil	Peanut oil, arachis oil	Cottonseed oil	Sesame oil
Source Raw material	From the flesh and kernels of the fruits of the olive tree, the oil from kernels being known as olive kernel oil	From rape seed and several varieties of brassica campestris	Seeds of black and of white mustard	Seeds of Ricinus communis	Peanuts, Leguminose arachis hypogæa	Seeds of cotton, Gossypium herbaceum	Seeds of Sesamum orientale and indicum
Per cent of oil in seeds, etc.	Flesh 56, Kernel 12	33–43	Black mustard 15–25; white mustard, 25–35	50–60	Kernels 38–50 Husks 4.4	20–25	47–56
Preparation of the crude oil, purification and uses	The olives are pressed with the kernels or without these. The marc is first pressed cold, then warm with gradually increasing pressure. The edible oils ("Provence oil," "Virgin oils," etc.) are obtained by pressing cold, the oils for technical use by pressing warm. By extracting the residues in the presses with carbon disulphide, still poorer grades (sulphur oils) are obtained. Lavate oils are obtained by treatment of the pressed material with hot water. Many other products are obtained by fermentations, and by other means. Tournant oils contain considerable oleic acid; they are obtained from the fermented marc of pressed olives. The tournant oils form emulsions with carbonates of the alkali metals which determines their application as turkey-red oils	As a rule by pressing. The press cakes still contain, after 2–3 pressings, from 7.5 to 10.1 per cent of oil. To refine, one per cent of sulphuric acid, 70 per cent of water at 50° C. and 1.5 per cent of milk of lime are added. Instead of washing with milk of lime pure water may be used. Filtration and decolorization with bone-black may be resorted to. Crude rape oil is used mainly for lubrication, refined oil is used for burning	By pressure or extraction. The press cakes are worked up for ethereal mustard oil, by stirring with warm water and then distilling after standing a long time. Black mustard oil gives allyl mustard oil (C_3H_5CNS); white mustard oil gives sinalbin mustard oil, C_7H_7OCNS. The fatty oil is used as a lubricant, for manufacture of soap and as a burning oil	Generally by pressure, rarely by extraction. The seeds are heated to 80° C. before pressing. The second and third pressings give darker, less valuable oils. For extraction, carbon disulphide or alcohol, but not naphtha, may be used since the oil is insoluble in the latter. To separate mucin and vegetable protein, it is boiled with water, allowed to settle away from air and light and clarified by filtration through bone-black	Like sesame oil. The best cold-pressed oils are used as edible oils; they are colorless; second quality is pale yellow. The odor and taste is like that of the best "Provence oil." Is used in manufacture of margarine	The kernels, freed from cotton and husks, after grinding to a meal and heating, are pressed. The crude deep brown-red oil is purified by treatment with 10–15 per cent sodium hydroxide, whereby the coloring matter and slimy materials are precipitated with the soap formed (soap stock). The further clarification is brought about with fuller's earth. The oil is used in the manufacture of oleomargarine and cottolene (artificial lard)	Generally by three pressings, one cold, two hot. The cold pressed oil is used as an edible oil. The oil from the third pressing (as well as that extracted by solvents) is used in manufacture of soap. The German regulations require that sesame oil be added to oleomargarine in order that it be readily detected

German Sources of Fat

The question of finding substitutes for fat became a serious problem for Germany during the war. Fats have not been prepared synthetically by methods satisfactory for quantity production. The prospect of an immediate solution of this problem did not seem promising, so that more attention was paid to stock-raising and the judicious use of chemical fertilizers as a means of increasing the amount of fat available. As a means of partially meeting the requirements, the following measures were adopted in Germany wherever possible:

1. Butter and margarine were rationed; in this way the decreased amount available was apportioned uniformly among the population. The use of marmalades was encouraged as the sugar contained might well be considered as a fat substitute, as sugar provides over four large calories per gram consumed.

2. Hydrolysis of fat for the production of soap was forbidden. In this way no fat, which might have been used for margarine was used for soap; furthermore for making soap only fatty acids from which glycerine had been completely removed were used.

3. The use of oils (such as linseed) which might be used as food was not permitted for varnish, linoleum, or paints. As a substitute for varnish was suggested the use of cumarone resins or synthetic resins made from phenol and formaldehyde; the production of linoleum was, for the time being, suspended.

4. The use of clay washing compounds, of washing powders containing little soap, and of various colloidal inorganic soap substitutes (page 475 and 468) was encouraged; this reduced the consumption of fat for washing purposes to a minimum.

5. Fish oils were hydrogenated by the catalytic method; in this way were obtained solid fats usable as food.

6. Much oil was obtained by extraction from the embryos of wheat, rye, barley and oats (which represent from 2 to 4 per cent of the grain, in the case of corn from 10 to 14 per cent) which are separated by mechanical milling processes from the rest of the grain. The embryo of corn contains 12 per cent of fat and 35 per cent of protein, the former being used as a salad oil and for the production of margarine, the latter being a valuable food for cattle.

7. Oil was recovered from various seeds and fruits which during a time of normal import could not be economically treated for fat: sunflower seed, beech nuts, cherry stones, grape seeds, plum stones, walnuts. Cherry stones yielded about 3.25 per cent, plum stones 4.3 to

6.8 per cent, grape seeds (4850 tons collected in Germany and Austro-Hungary) gave 8 to 20 per cent of oil.*

8. Increased cultivation of plants gave increased yields of rape seed, linseed, hedge mustard, and soja beans, all capable of yielding oil.

9. Recovery of fat from waste waters of slaughter houses, sausage factories, barracks, hospitals, and hotels was accomplished by various devices.† The material collected contained about 40 per cent of fat.

10. Fat was also recovered from the sewage of large cities; this was done in the clarification tanks or by special mechanical separators.‡ Before the war there was needlessly lost from 3 to 4 kilograms of fat per person per year (in Berlin this went as high as 7 kilos.). With a diminished use of fat in the household, these figures do not hold. The fat recovered contains unsaponifiable material due to the considerable amounts of lubricating oils and other mineral oils which originate in various industrial establishments.

11. Very important was the recovery of fat from bones. This recovery was carefully organized. The fresh bones from slaughter houses contained about 16 per cent of fat; the bones were pulverized, heated with steam under 4 to 5 atmospheres pressure, whereby a soup stock was also collected. The residue was used as fertilizer. In the invaded territories the recovery of fat was carried on systematically. From the bones which were not obtained in a fresh condition, bone oil was obtained by extraction with solvents, this material being worked up into stearin, olein, glycerine, and pitch.

12. Fat was obtained by P. Lindner by the growth of a fungus obtained from a sample of the sap of the birch. The fungus converted the sugar of the sap into fat; it converts other sugars into fat, without alcoholic fermentation, but part of the sugar is used in the formation of protein and mucins. An attempt was made to grow this fungus in quantity.

13. Fats and oils were replaced in various industrial uses by various substitutes. In greases soap was replaced by montan wax soaps, in the manufacture of leather, fish oils were displaced by mineral oils. Mineral oils were also used as cutting oils, and in tempering metals.

14. Attempts were made to produce fatty acids from lignite-tar

* Chem. Umschau, **22**, 102 (1915); **23**, 20 (1916).

† Seifensiederztg., **42**, 662, 846 (1915). D. R. P. 287432, 631898, 631899.

‡ Chem. Ztg., **39**, 792 (1915); Z. angewandte Chem., **28**, 685 (1915); also **12**, **849** (1899); **21**, 1315 (1908).

oils by ozonizing them. Paraffin is said to have been oxidized at high temperatures into fatty acids. The yield has not been stated.*

VIII. Methods for the Separation of the Fats into their Separate Components

The following methods have been used in the scientific study of certain questions concerned with the chemistry of fats; the industrial methods of fat and oil analysis are discussed in Section IX.

(*a*) **Solid from Liquid Acids. 1. The Method of Varrentrap** depends on the easy solubility in ether of the lead salts of the unsaturated acids.

3 grams of fat are saponified with 50 c.c. of alcoholic potash; the solution is acidified with acetic acid, exactly neutralized with N/10 sodium hydroxide and then diluted with 50 c.c. of water. From this solution, the lead salts are precipitated by gradually adding a mixture of 30 c.c. of 10 per cent lead acetate in 200 c.c. of water; the supernatant liquid is passed through a filter after cooling, the crystals of lead soap are washed with hot water, drained as completely as possible and finally the last traces of water are removed with filter paper. It is necessary to dry the lead soaps to prevent oxidation.

The lead soaps are then shaken with 150 c.c. ether, at first cold, later warmed gently under a reflux condenser. The insoluble lead soaps are separated by filtration and then washed with 30 c.c. portions of ether till the filtrate on evaporation and decomposition of the residue with dilute hydrochloric acid is seen to contain only solid (and not oily) acids. The united ether extracts are shaken with excess dilute hydrochloric acid, washed free from lead salts and mineral acids, and the ether is then distilled (this last operation should be carried on in a stream of hydrogen if the acids are decidedly unsaturated).

To separate the solid acids, the ether-insoluble soaps are warmed with naphtha and hydrochloric acid, with frequent shaking, until the naphtha solution is clear. To complete the decomposition, the material is twice shaken with hot hydrochloric acid, then washed free from mineral acid and after distilling off the naphtha, the residue is weighed. The solid acids are not completely separated from the liquid by this method, a small amount of liquid remaining with the solid, and vice versa. Thus the solid acids from olive oil had an iodine number of 3.6, from datura oil 3.7, corresponding to 3.4 per cent of liquid acid. A quantitative separation is prevented† by the formation of mixtures of lead soaps of solid and liquid acids. The amount of the solid acids, as well as the iodine value, should be stated to give an idea as to the amount of liquid acid present.

In the examination of fats containing a high percentage of acids soluble in water (butter), it is well to remember that lead soaps of these acids are soluble in ether, and that therefore the liquid acids ob-

* Z. angewandte Chem., **31**, 69, 115, 148 (1918).

† Partheil and Ferié, Archiv. f. Pharmacie, **1903**, 552.

tained will always contain saturated acids of low molecular weight. To separate the unsaturated acids from the fats mentioned, the liquid acids, as obtained above, may be exhaustively extracted with water; or one may start in the first place with acids insoluble in water.

The method of Varrentrap is not applicable in the presence of erucic (in rape oil) or iso-oleic acid (in candle stock), since the lead salts of these acids are difficultly soluble in ether.

2. **Method of Farnsteiner.***

About 4 grams of the sample are saponified in a 300 c.c. Erlenmeyer flask with 50 c.c. of N/2 alcoholic KOH in a stream of hydrogen; the hot solution is neutralized with acetic acid (phenolphthalein). To the neutral solution, a mixture of 30 c.c. of 10 per cent lead acetate in 150 c.c. of water is slowly added; the precipitated lead soaps are made to attach themselves to the walls of the beaker by vigorous shaking and by cooling under a water tap. The lead soaps are then washed with hot water and dried in a stream of hydrogen; the dry lead soaps are dissolved in 200 c.c. of boiling, thiophene-free benzol (still in a stream of hydrogen), the solution is kept two hours in an ice chest at 8° and the precipitated lead salts are then filtered off. The filter is extracted with 15 c.c. of benzol and leached with 10 c.c. more (in a stream of hydrogen). These 25 c.c. are united and cooled. The crystallized lead salts are treated twice more in this way. The filtered benzol solutions are united (275 c.c.) and the iodine number of the liquid acids (liberated by HCl) is determined as on page 410 (Hubl).

The lead soaps remaining on the paper after the last recrystallization are treated with a mixture of equal parts of fuming hydrochloric acid and alcohol and then washed into a separatory funnel, first with alcohol, then with ether. After adding water, an ether extraction is made; the ether solution is dried with calcium chloride; after filtering and distilling off the ether, the solid fatty acids are dried in hydrogen at 105°. The content of liquid acid in the solid can be estimated from the iodine value.

3. **Method of Facchini and Doria** (page 389). On treatment with acetone (90 per cent) the potassium salts of unsaturated acids dissolve, the other salts are insoluble. The oxidation is slight and the separation quite sharp† (better than the Varrentrap method), so that the solid fatty acids give a lower iodine value, the liquid acids a higher iodine value.

4. **Separation of Large Amounts of Solid Acids, knowing approximately the Amount Present.** The following method may be used in the preparation of solid acids for experimental work.

The separated total fatty acids (prepared in the usual manner) are dissolved in 90 per cent alcohol (for every 10 grams of acid, 50 c.c. of alcohol) and precipitated with insufficient alcoholic lead acetate solution so that only the lead salts of the solid acids, which form first, will precipitate.

* Zeit. f. Nahr.-u. Genussmitt., **1898**, 390.

† Z. angewandte Chem., **28**, II, 297 (1915).

To separate the solid acids from peanut oil (arachis oil), which contains about 10 per cent of saturated acids, in order to make the test for arachidic acid, 10 grams of fatty acid are treated with 1 gram of lead acetate (this corresponding to about 15 per cent of fatty acid). The resulting precipitate is then collected by suction, recrystallized from benzol and decomposed as under 1 (see also page 388).

(*b*) **Quantitative Determination of Stearic Acid in Fatty Acid Mixtures.** The procedure* depends on the fact that stearic acid is insoluble in a solution saturated with stearic acid at 0°, while palmitic, myristic and oleic acids are soluble.

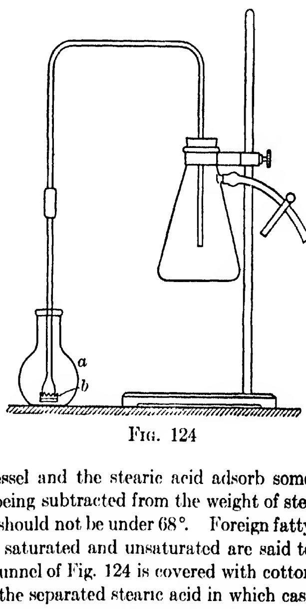


FIG. 124

0.5 gram of the sample, if solid (5 gram if liquid), is dissolved in 100 c.c. of a saturated solution of stearic acid† in 95 per cent alcohol in a 150 c.c. flask under a reflux. The solution obtained is kept over night at 0° in an ice chest. To facilitate the crystallization the flask is shaken the next day in ice water, in which it remains then for ½ hour. The supernatant liquid is then sucked from the precipitate by the arrangement of Fig. 124; the width of *b* should be not more than 6 mm. The filtrate should be clear; the residue is washed three times with 10 c.c. portions of the saturated stearic acid solution at 0°. The residue is then dissolved in hot alcohol, the alcohol evaporated and the residue weighed. Since the walls of the vessel and the stearic acid adsorb some solution, a correction is made, 0.005 gram being subtracted from the weight of stearic acid. The melting point of the product should not be under 68°. Foreign fatty acids of all kinds, volatile and non-volatile, saturated and unsaturated are said to have no effect on the result.‡ The suction funnel of Fig. 124 is covered with cotton cloth which may easily become clogged by the separated stearic acid in which case it may be advisable to use the filtering arrangement described on page 109.

The method described is said to be nearly quantitative§ in the presence of at least 0.1 gram of stearic acid but if less is present, the values are very inexact owing to supersaturation phenomena.

If the solid fatty acids separated according to page 371 contain only palmitic and stearic acids their amount can be estimated from the average molecular weight (page 401) and the known molecular

* Hehner and Mitchell, Analyst, **21**, 316 (1896).

† The saturated solution is made by dissolving 3 grams of stearic acid in a liter of warm alcohol, cooling in an ice chest over night and then filtering with the help of the apparatus sketched in Fig. 124.

‡ This is, however, not true for arachidic acid, lignoceric acid and other acids melting higher than stearic acid (see page 388).

§ Kreis and Haffner, Zeit. f. Unters. d. Nahr. -u. Genussmit., **1903**, 22.

weights of palmitic and stearic acids. If x per cent of the acid of molecular weight m_1 and y per cent of the acid of molecular weight m_2 are present and the average molecular weight of the mixture is m then

$$x + y = 100$$
$$\frac{x}{m_1} + \frac{y}{m_2} = \frac{100}{m},$$

it follows that

$$x = \frac{100\, m_1\,(m - m_2)}{m(m_1 - m_2)} \qquad y = \frac{100\, m_2\,(m_1 - m)}{m(m_1 - m_2)}.$$

(*c*) **Examination of the Liquid Acids Obtained by the above Methods.** The nature and amount of unknown liquid acids is sometimes to be determined. In general oleic, linoleic and linolenic acids are to be considered.

1. **Iodine Value.** The amount of oleic or more unsaturated acids can be approximately determined from the iodine number (see page 406). The iodine value of the liquid acids is known as the inner iodine value.* Tolman and Munson † calculate the inner (or true) iodine value by the formula

$$A = \frac{(J)\,(100)}{L},$$

where

A is the iodine number of the liquid fatty acids,
J is the iodine number of neutral fat,
L is the per cent of liquid acids in the neutral fat, that is, total fatty acids (95.5) less the solid acids.

For pure unsaturated acids the following iodine values can be calculated (Benedikt-Ulzer):

TABLE 87

Acid	Formula	100 grams of acid add g grams of iodine (iodine value)
Hypogaeic acid	$C_{16}H_{30}O_2$	99.88
Oleic and iso-oleic acids	$C_{18}H_{34}O_2$	89.96
Erucic	$C_{22}H_{42}O_2$	75.05
Ricinoleic	$C_{18}H_{34}O_3$	85.14
Linoleic	$C_{18}H_{32}O_2$	181.22
Linolenic	$C_{18}H_{30}O_2$	273.80
Clupanodonic	$C_{18}H_{28}O_2$	368.70

* Wallenstein and Fink, Chem. Ztg., **18**, 1190 (1894).
† Chem. Zentrallb., **1903**, II, 1288.

2. **Separation According to Hazura.*** This method depends on the fact that these acids take up two hydroxyl groups on oxidation in alkaline solution with potassium permanganate forming oxyacids with characteristic properties.

Oleic acid	gives dioxystearic acid	melting point, 136.5°.
Linoleic acid	gives sativic acid	melting point, 174°.
Linolenic acid	gives linusic acid	melting point, 204°.
Isolinolenic	gives isolinusic acid	melting point, 174°.

These oxyacids differ decidedly in their behavior towards solvents (water and ether).

The method of oxidation.

30 grams of liquid acids are saponified with 36 c.c. of KOH (sp. gr. 1.27), then diluted to 2 liters with water; to this solution are added two liters of a 1.5 per cent solution of potassium permanganate, stirring constantly (with fish oils it is necessary to cool to 0° and a 0.5 per cent solution should be used). After standing 10 minutes, aqueous sulphurous acid is added to dissolve completely the precipitated manganese dioxide.

(α) **The Oxidation Products Insoluble in Water.** The precipitate formed by the mineral acids may contain unattacked fatty acids, dioxystearic acid and sativic acid.

The unoxidized acids in the precipitate are easily separated from the oxidized acids with naphtha (boiling point under 50°), which does not dissolve oxyacids. The undissolved acids are treated with ether at room temperature (for 20 grams acid, 2 liters of ether).† Dioxystearic acid goes into solution; it is purified by repeated recrystallization from 96 per cent alcohol; sativic acid remains undissolved, and is crystallized from hot water. Traces of dioxystearic acid sometimes remain insoluble in the water.

(β) **Oxidation Products Soluble in Water.** The filtrate from the precipitate, which may contain linusic acid and iso-linusic acid, is neutralized with KOH, evaporated to $\frac{1}{12}$ its volume and acidified. The flocculent brown precipitate forming in the presence of the latter acid is extracted dry with ether to remove azelaic acid and other secondary oxidation products. The insoluble acids are recrystallized from alcohol. Microscopic examination of the crystals may determine whether only linusic or also iso-linusic acid is present; the former gives truncated rhombic plates, the latter gives needles. The two can be separated by recrystallization from a little water; iso-linusic acid remains in the mother liquor.

The method described gives only approximately quantitative results regarding the composition of a mixture of liquid acids since a part of the acids used undergo deep-seated changes.

3. **Determination of the Liquid Acids by Means of the Bromine Addition Products.** The unsaturated acids, in mixtures may be char-

* Monatshefte, **1887**, 147, 156, 269; **1888**, 180, 198, 469, 941, 947; **1889**, 190.

† Best by direct extraction in a Soxhlet apparatus. Chem. Umschau., **22**, 15 (1915).

acterized by their different behavior towards bromine.* By the action of an excess of bromine the following products are obtained:
linolenic acid gives hexabromstearic acid, melting point 180–181°;
isolinolenic acid gives liquid hexabromstearic acid;
linoleic acid gives tetrabromstearic acid, melting point 113–114°;
oleic acid gives liquid dibromstearic acid;
clupanodonic acid gives octobromstearic acid, melting point over 200°.

The brominated acids show considerable differences in solubility (see page 392 and page 414).

(α) **Bromination According to Hehner and Mitchell.** 0.3 gram of fatty acid is dissolved in 10 c.c. of glacial acetic acid; the solution is cooled to 5° and bromine added drop by drop until the red color persists. After standing 3 hours at 5° it is filtered through asbestos or a pleated filter and washed in succession with 5-c.c. portions of cooled glacial acetic acid, alcohol and ether. There remains in solution dibromstearic acid; the mixture of hexabrom- and tetrabrom-stearic acid is insoluble. This mixture is dried, weighed and its bromine content determined. Since a hexabromide should contain by theory 63.32 per cent and a tetrabromide 53.33 per cent bromine, the amounts of the separate acids may be calculated from the following:

$$x + y = 100$$

$$\frac{63.3\,x}{100} + \frac{53.3\,y}{100} = B \qquad x = (10)\,(B - 53.3),$$

where x is the per cent of hexabromide, y that of the tetrabromide and B the per cent of bromine in the crude mixture. The melting point of the mixture should be about 175 to 180°. 1 gram tetrabromstearic acid corresponds to 0.4666 gram linoleic, while 1 gram of hexabromstearic acid corresponds to 0.3667 gram of linolenic acid. If the fatty acids from oils of marine animals are under examination, the precipitate will contain also some octo-bromstearic acid besides the tetra- and hexa-acids. The octa-acids can be recognized by having a melting point over 180° and by blackening at 200°. In the presence of octa-bromide the content of tetrabromide cannot be estimated by determining the bromine. If a mixture of hexa- and octa-bromides is suspected, the bromides are separated by boiling with benzol in which the octa-bromide is insoluble.

(β) **Bromination by the Method of Farnsteiner.** To identify linoleic acid in the presence of oleic and in a mixture free from linolenic acid, 1 gram of acid in 10 c.c. of chloroform (or the filtrate from α, containing dibromoleic acid and tetrabromlinoleic acid) is treated with 1 gram of bromine in 10 c.c. of chloroform; after several hours' standing, the solvent is distilled and the residue treated with low boiling (35 to 68°) naphtha in which the dibromide is easily, the tetrabromide only slightly, soluble. On cooling the naphtha solution, the tetrabromide will almost completely precipitate and can be identified by the melting point of 113 to 114° and molecular weight of 600.

Both of the methods described require further study.

* Hazura, Monatshefte, **1887**, 463, 472; Hehner and Mitchell, Analyst, **1898**, 313; Farnsteiner, Ztschr. f. Unt. d. Nahr.-u. Genussmit., **1899**, 1.

4. **Separation of Linoleic and Linolenic Acids from Oleic Acid According to Farnsteiner.*** Barium oleate is little soluble in cold aqueous benzol-alcohol, while the barium salts of unsaturated acids $C_nH_{2n-4}O_2$ and $C_nH_{2n-6}O_2$ are easily soluble. By means of this, Farnsteiner found oleic acid in linseed oil (Mulder had previously assumed it present).

5. **Hydrogen Value, Preparation and Determination of the Constitution of Linseed Acids According to Erdmann and Bedford.**† According to these authors a modification of the method of Sabatier and Senderens‡ is used to add hydrogen quantitatively to liquid acids (which do not easily volatilize or which decompose on volatilization) or their esters. The weighed substances to be reduced are dropped through a vertical glass tube heated to 170 to 200° and filled with pumice stone covered with prepared nickel, a stream of hydrogen (measured) passing at the same time. After the treatment in the presence of the catalytic agent, nickel, the excess hydrogen is quantitatively determined by changing it into water as in an elementary analysis. The hydrogen number is given as the amount of hydrogen absorbed by 100 grams of substance.

Oleic acid was thus quantitatively converted into stearic acid, crotonic ethyl ester into the ethyl ester of butyric acid and the ethyl esters of linoleic acids into the ethyl ester of stearic acid. This latter transformation shows that linoleic acids contain a normal straight carbon chain.

The acid in linseed oil which gave a solid hexabromide (M. P. 179°) was called α-linolenic acid; from the amount of bromide and of the ethyl ester of linolenic acid (22.3 per cent) they calculated that 15.3 per cent of linolenic acid was present in the acid. The authors prepared the potassium and barium salts, as well as the ethyl ester, of the hexabromstearic acid.

The bromine of the hexabrom-acid and ester is easily removed by treatment with feathered zinc and alcohol; in the former case some zinc salt and some ethyl ester of linolenic acid are formed. From the mixture precipitated with water, the zinc is removed with sulphuric acid; the separated oil is saponified. The separated acids are dried in ether solution with anhydrous sodium sulphate and distilled in vacuum. The acid passes at 0.001 to 0.002 mm. pressure (with a 75 mm. column of vapor) between 157° and 158° as a colorless oil with not unpleasant odor. The linolenic acid obtained by reduction of the hexabromide is a mixture of α- and β-linolenic acids.

* Ztschr. f. Unters. d. Nahr. u. Genussmit., **1899,** 1; **1903,** 161.

† Ber., **42,** 1324 (1909); Inaugural Dissertation of Bedford "Ueber die ungesättigten Sauren des Leinöls."

‡ Ann. chim. phys., **4,** 319 (1905).

E. Erdmann, Bedford and Raspe,* using the method of Harries,† were able to convert the linseed acid (like oleic acid), according to the solvent (hexahydrotoluol or chloroform), into a normal ozonide with 9 atoms of oxygen or into linolenic acid ozonide peroxide with 10 atoms of of oxygen per gram molecule. The peroxide of α- (and of β-) linolenic acid ozonide gives on treatment with water the half aldehyde of azelaic acid. Similar changes took place with the ethyl ester. The ozonide peroxides of the esters have different velocities of decomposition in water but give the same products. α- and β- linolenic acids are stereoisomeric like oleic and elaidic acids.

(*d*) **Separation of Solid Acids from Each Other. 1. Fractional Precipitation According to Heintz.**‡ If an alcoholic solution of a mixture of saturated fatty acids is fractionally precipitated with magnesium acetate, the magnesium salts of the acids of high carbon content are first precipitated. By systematic precipitation of the various fractions, acids with decreasing molecular weights are obtained. The method is especially applicable to acids which form constant melting mixtures, such as the molecular mixture of stearic and palmitic acids, known formerly as margaric acid. Heintz showed it to be a mixture by this method. The datura acids of Gerard from datura oil and the acid of formula $C_{17}H_{34}O_2$ from palm oil, found by Nordlinger, were shown§ to be mixtures of at least three acids; recently, however, Meyer and Beer,|| by exhaustive fractionation of lithium salts, proved the presence of 2.5 per cent of an acid $C_{17}H_{34}O_2$ in datura oil (see below) which was identical with margaric acid as prepared by Krafft and had a melting point of 59 to 59.5°.

1.5 grams of the acid are dissolved in alcohol and precipitated hot by an alcoholic solution containing from 0.04 to 0.05 gram of magnesium acetate. After separating the precipitate, the free acid in the filtrate is neutralized with ammonia and then again a like amount of magnesium acetate is added. In crystallizing, the temperature should not be too low since otherwise some fatty acid will also precipitate. The acids are liberated from the separate precipitates and tested for melting point and molecular weight. A quantitative separation by this method is not possible.

2. Meyer and Beer used the following method:

100 grams of oil were emulsified with 500 c.c. of 95 per cent alcohol, treated at boiling temperature with 10 grams lithium oxide in 30 c.c. of water and boiled one hour under a reflux condenser. The lithium salts separating on cooling were sucked

* Ber., **42,** 1334 (1909).

† Ber., **39,** 3667 (1906).

‡ J. f. prakt. Chem., **1855,** 3.

§ Holde, Ubbelohde dan Marcusson, Mitteilungen, **23,** 36 (1905); Ber., **38,** 1247 (1905).

|| Monatshefte, **33,** 311 (1912).

dry, washed with alcohol and freed from unsaturated acids by the method of Farnsteiner (see page 372) by the use of lead salts. The lead salts were rubbed up with concentrated hydrochloric acid, put into hot water and heated. The acids obtained on cooling, washing, drying and powdering (140 grams) were dissolved in 96 per cent alcohol and shaken with 5 c.c. of a 10 per cent alcoholic lithium acetate solution and a few drops of ammonia water. The salts separating cold were washed with cold alcohol, treated with hydrochloric acid, washed free from mineral acid and recrystallized from 75 per cent alcohol. When the lithium acetate gave no more precipitate, then magnesium acetate and finally barium acetate was used to bring about precipitation. All fractions melting at 59 to 59.5° with a molecular weight of 269.2 to 271.4 were united and again fractionally precipitated with lithium acetate, every precipitate after decomposition being fractionated from alcohol, and every single partial fraction recrystallized from petroleum ether and benzol. Melting point and molecular weight remained unchanged, likewise after fractionation with magnesium and barium acetates. For this reason it seems likely that daturic acid is really a chemical individual, namely, heptadecylic acid, of melting point 59.5 to 60° and with a molecular weight 270.3, these being the same values obtained by Krafft* with synthetic heptadecylic acid.

3. **Fractional Distillation in a Vacuum.** Fractional distillation is a much more rapid method of separating the components of a mixture. Generally a vacuum of 15 mm. is sufficient but at times decomposition of acids will occur. This can be entirely prevented by distillation in an absolute vacuum,† obtained by using a mercury pump.‡ The rotating oil pump of Dr. Gaede-Freiberg is to be recommended for vacuum distillations.

Boiling Points of Higher Saturated Fatty Acids in an Absolute Vacuum

Lauric acid	102° C.
Myristic acid	121 to 122° C.
Palmitic acid	138 to 139° C.
Stearic acid	154.5 to 155.5° C.

4. Holland§ esterifies 100 c.c. of fatty acid by boiling for half an hour with 100 c.c. of alcohol and 10 c.c. of conc. hydrochloric acid; the esters are then separated by vacuum distillation. To decompose the esters, a glycerine solution of alkali is used. In the dissolving and crystallizing of the fatty acids, care must be taken to prevent esterification.

5. Morelli|| considers a separation of stearic, palmitic and oleic acids possible through the differing solubility of their hydroxamic acids. The hydroxamic acids

* Ber., **12**, 1672 (1879).

† Krafft, Ber., **15**, 1692 (1882); **22**, 816 (1889).

‡ Ubbelohde, Zeit. f. angew. Chem., **19**, 2240 (1906).

§ Zeit. f. angew. Chem., **24**, 1054 (1911).

|| Chem. Zentralblatt, **12**, 1019 (1908).

were first obtained * by the action of hydroxylamine on esters (of monatomic alcohols). The glycerides act similarly.

$$C_6H_5 \cdot COOC_2H_5 + NH_2OH \rightarrow C_6H_5C\,(:NOH)OH + C_2H_5OH.$$

(e) Preparation of Pure Glycerides of Saturated Acids from Natural Fats

1. **Mixed Solid Glycerides.** These have been obtained from solid fats† (mkani fat, cacao butter) by crystallization from solvents like ether, and acetone, at room temperature. From olive oil have been obtained solid glycerides melting at + 30°; these substances were separated by cooling the ether-solution of the oil to − 50° or − 60°, by means of solid carbon dioxide and alcohol, the precipitated glycerides being repeatedly recrystallized.

2. 1 to 2 grams of fat ‡ are dissolved in 2 or 3 volumes of ether, chloroform or benzol and from this solution, four portions are crystallized by gradually lowering the temperature. Each fraction is in turn separated into four fractions. Instead of lowering the temperature, the solubility may also be decreased by adding alcohol. Fractions melting within 5° are to be united. To separate the glycerides containing oleic acid, the products are treated with Wijs ICl in glacial acetic acid § whereby the oleic derivatives are changed to ICl derivatives. The purified glycerides are then fractionally dissolved, by which method tristearin was obtained as the least soluble glyceride of mutton tallow.

To obtain other glycerides, the mother liquors obtained by fractional precipitation (in so far as they contain glycerides of the same melting point) are united and the substances again fractionally precipitated. The difference in melting point is two degrees in the first fractionation and becomes one degree in the second fractionation and 0.5 in the third and fourth. To determine the melting point, the glycerides separating from solution are to be used. The glycerides thus obtained may be considered as pure when they no longer give the halogen reaction with copper oxide and when the melting points of the substances crystallized from benzol and from the solidified fused mass are the same.

IX. Industrial Physical and Chemical Tests

(a) *Determination of the Fat Content of Seeds, Oil-Cakes, etc.*

In the laboratory the amount of oil in seeds is determined as follows: 100 grams of finely-ground, air-dried material are extracted in an S. & S. extraction thimble (see page 107) with petroleum ether or carbon tetrachloride; this may take 6 hours. Very fatty or gummy substances may be mixed to advantage with sand;

* Jeanrenaud, Ber., **22**, 1270 (1889).

† Chem. Umschau., **6**, 45, 91 (1899). Arb. a. d. Kaiserl. Gesundheitsamt, **1896**, 540; **1897**, 306; **1901**, 371. Z. Nahr. u. Genussm., 1, 641 (1904); **25**, 322 (1913). Chem. Ztg., **37**, 890 (1913); **38**, 844 (1914). Berichte, **34**, 2402 (1901).

‡ Bömer, Zeit. f. Unt. d. Nahr. u. Genussmit., **17**, 353 to 396 (1909).

§ Kreis and Haffner, ibid., **7**, 641.

or after extraction of nearly all the oil, the mass is reground to open up the last cells containing oil. If ethyl ether is used it is better to dry the substance previously and then use anhydrous ether, since moist seeds or cakes easily give up impurities to the ether. Materials containing drying oils must be carefully dehydrated (linseed or cakes) since the oils at high temperature or too long heating become partially insoluble. The extracts of samples not thoroughly dried are often dark in color and contain resinous material.

After extraction, the solution is filtered, distilled and the residue of crude fat dried and weighed. Table 86 (page 368) gives some data regarding the fat content of certain seeds. Since ether dissolves some non-fatty substances besides some water from moist materials, after distilling off the ether, the fat is separated from these bodies by solution in petroleum ether. Since fats with high iodine values cannot be dried at 105° without change of substance, a stream of hydrogen or carbon dioxide is passed over the fat during the drying.

The fats and the coloring materials associated with them are more soluble in benzol, carbon tetrachloride, trichlorethylene and carbon disulphide, than they are in petroleum ether; extracts in benzol for example are therefore more darkly colored.

(b) *Physical Tests*

1. **Solubility.** All oils and fats are easily soluble in ethyl ether, chloroform, carbon disulphide and, with the exception of castor oil, also in petroleum ether and mineral oils. Most of the fats are only slightly soluble in absolute alcohol; the solubility becomes greater as the amount of fatty acid contained becomes greater, fatty acids being easily soluble in alcohol. As a consequence, commercial palm fat, which is often almost completely split into fatty acid, is easily soluble in alcohol. Moreover, castor oil and grape-seed oil are soluble in all proportions in alcohol. Dolphin oil and porpoise oil, as well as butter fat and similar fats and oils, which contain glycerides of acids of low molecular weight, are generally appreciably soluble in alcohol. The differing solubilities of the fats in alcohol and in glacial acetic acid may be used to a certain degree in analytical work.

The best solvents for fats are chloroform and carbon tetrachloride and these are used in chemical cleansing establishments for removing old grease spots, etc.; unfortunately these are also the most expensive. The present tendency of the trade is to replace the highly inflammable solvents for fats, such as naphtha, benzol and carbon disulphide, with the practically incombustible carbon tetrachloride and trichlorethylene. In practice, the former has the disadvantage of gradually attacking the metal apparatus, especially copper; and furthermore both of the chlorinated bodies have a high specific gravity and are therefore more expensive, volume for volume. Fats and fatty acids also dissolve in anilin.*

* See D. R. P. 302,210.

(2) **Specific Gravity and Coëfficient of Expansion.** The specific gravity of fats ranges from 0.913 to 0.996. The non-drying oils, such as olive oil and neat's-foot oil, as well as the crucifers, rape-seed and mustard oils, have the lowest specific gravity, 0.913 to 0.916. The specific gravity increases quite regularly with the iodine number. Castor oil, grape-seed oil and croton oil, because of their peculiar composition, have the highest specific gravity observed in liquid fats, 0.955 to 0.9734. Solid fats have specific gravities ranging from 0.920 to 0.970. Liquid waxes have values between 0.876 and 0.883, while those of solid waxes fall in between 0.960 and 0.999.

The specific gravity of liquid products is determined as described on page 2; solid fats and waxes are tested by the alcohol-flotation method of page 4 or by means of the Westphal balance, generally at 100°, as shown in the diagram (Fig. 4). The Sprengel pycknometer (page 4) is also used.

The coefficient of expansion of fatty oils and waxes, which is of importance in the calculation of the specific gravity, ranges from 0.000654 to 0.000838. The change of the specific gravity with the temperature (sp. gr. × coefficient of expansion) is on the average ±0.0007 for one degree change in temperature. In Table 88 are given the recalculation factors for several fats and waxes.*

TABLE 88

Material	Factor for 1° rise in temp.	Material	Factor for 1° rise in temp.
Cottonseed oil	0 000677	Olive oil	0.000729
Beeswax	0 000838	Palm-nut oil	0 000701
Butter	0 000664	Palm oil	0 000727
Arachis (peanut) oil	0 000675	Castor oil	0.000690
Japan wax	0 000734	Seal oil	0 000654
Cocoa butter	0.000772	Rapeseed oil	0 000675
Neat's-foot oil	0 000671	Lard oil	0 000703
Cocoanut oil	0 000686	Sesame oil	0.000687
Cod-liver oil	0 000685	Sunflower oil	0 000746
Linseed oil	0 000690	Sperm oil	0.000815
Menhaden oil	0 000698	Tallow	0.000727
Poppy-seed oil	0 000744	Whale oil	0.000745

(3) **Melting Point.** Since the fats are complicated mixtures, their melting points are not so sharp as those of definite chemical substances. On warming, the fats soften, become translucent and finally clear when melted; but since these changes are not sharp, the beginning and end of the melting are determined.

* Ubbelohde, Bd. I. 309.

For the determination and meaning of the melting point, see page 36.

(4) **Solidification Point. Liquid Fats.** The solidification point of fatty oils is determined only in test tubes (see page 34) not in a U-tube. In general, stirring of fatty oils favors their solidification; in which respect they differ in property from mineral oils. To prevent supercooling in testing fatty oils, at least one sample should be stirred, at intervals, with a glass rod. The solidification temperatures of various oils are given in Tables 95 to 101. Solid fats, see page 37.

In analytical work, the solidification point of fatty acids, less frequently that of the fat itself, is used.

(α) **The Dalican Method** is much used in England, France and America. 50 grams of fat are saponified under a reflux condenser with 300 c.c. of N/1 alcoholic potash; after evaporation of the alcohol, and solution of the soaps in water, the fatty acids are precipitated by adding dilute sulphuric acid, the solution being then heated so that the fatty acids separate as an oily layer on top. They are separated by means of a separatory funnel and washed free from mineral acid with hot water. On heating the fatty acids on a water bath, some water and impurities separate; the warmed acids are then filtered through a dry paper in a hot-water funnel. A test tube 3.5 cm. wide and 16 cm. long is half filled with these acids and then supported in the neck of a wide-mouth bottle of colorless glass; a tenth-degree thermometer is then introduced with its bulb in the center of the mass of fatty acids. As soon as solidified particles appear in the bottom of the tube the fat is stirred with the thermometer three times to the right, three times to the left, without touching the sides, the thermometer being carefully observed meanwhile. The temperature, which is to be noted at intervals of say one minute, will first fall, then remain constant for some time or rise suddenly to a maximum, at which it remains stationary for some time, from which it again falls. The point at which it remains stationary is the solidifying point of the fatty acids. See page 37.

(β) **The Method of Wolfbauer** is used mainly in Austria. In this method the dried fatty acids (prepared in the usual manner) are run into a test tube 3.5 cm. wide, 15 cm. high, up to within 1.5 cm. from the top, the test tube being fixed in a wide-mouthed bottle of colorless glass. The cooling mixture is stirred with the thermometer till the originally clear liquid becomes opaque. From this point on the mercury is watched, its constant reading being taken as the solidification point.

(γ) **Method of Shukoff,** see page 37.

(δ) **Method of Finkener.*** In the methods from α to γ the solidification point is determined after stirring of the material; while in the Finkener method which is used in Germany by the customs officials to distinguish between tallow, lard and candle materials, the solidification point is determined in the previously unstirred mass.

If the solidification point is under 30° the material is a lard-like fat, if it lies between 30° and 45° the body is called a tallow, and if it comes

* Mitt., **7,** 27 (1889); **8,** 153 (1890); Chem. Ztg., **20,** 132 (1896).

over 45° the material is classified as candle material. However, pressed tallow, which is declared as such, even though it has a solidification point of 50°, is classified as tallow if it contains not more than five per cent of free fatty acid.

The Finkener apparatus consists of a rectangular wooden box with cover (Fig. 125) in which a glass flask of 49 to 50 mm. wide bulb is placed on a cork block; the flask carries a ground-in thermometer. The fat or fatty acid (separated as in α above) is kept molten for ten minutes in a porcelain dish on a water bath until clear and is then poured into the flask up to the mark, placed in the box, the cover put on and the temperature readings taken at intervals of two minutes. With hard fats the mercury begins to fall slowly, then remains stationary for several minutes, then rises to a maximum and then sinks again. The maximum is the solidification point. With softer fats, the temperature remains constant for some time at the solidification point, and then sinks without again reaching this temperature. In cases of doubt, the fat is remelted in the flask and the operation repeated. A regulation of the temperature is necessary only when it is much different from room temperature. The cooling of the fat from 100° to 50° takes about 45 minutes.

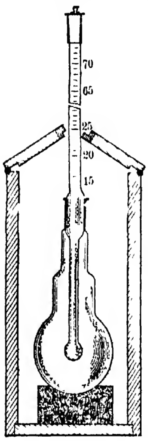


Fig. 125.

The Finkener method has the advantages of protecting the fatty material against the temperature effect of the outside air and also allowing the carrying on of several determinations at the same time; furthermore the dimensions of the apparatus and the position of the thermometer in the ground joint are fixed.

Comparisons* show that results of the methods of Wolfbauer and of Shukoff are identical, while those of Dalican and Finkener are somewhat lower (Table 89).

TABLE 89

	Solidification point	
	Dalican	Wolfbauer
Stearin	51 2	51.5
Mutton tallow	45 0	45 5
American neat's-foot oil	43 4	44.1
American neat's-foot oil	43.1	43.8
American neat's-foot oil	41.5	42.0
Russian neat's-foot oil	41.1	41.7
Russian neat's-foot oil	40 8	41.6

* Shukoff, Chem. Rev., 6, 12, (1899).

(5) **Specific Heat Capacity.** For the determination of the specific heat capacity see page 43. The specific heat capacity may be calculated by the method of Kopp by dividing the per cents of carbon, hydrogen and oxygen contained by their respective atomic weights and multiplying these quotients with the atomic heat capacities, 1.8 for carbon, 2.3 for hydrogen and 4.0 for oxygen. For poppy-seed oil which contains (Cloez) 77.5 per cent of carbon, 11.4 per cent of hydrogen and 11.1 per cent of oxygen, there can be calculated the specific heat capacity, 0.406.

TABLE 90

SPECIFIC HEAT CAPACITIES OF FATTY ACIDS*

	Temperature	Specific heat capacity
Butyric.	24 to 97	0 526
Capric, solid	0 to 16	0 697
Capric, liquid	35 to 103	0 524
Caprylic, solid	−11 to 8	0 630
Caprylic, liquid	16 to 90	0 545
Cerotic, solid	0 to 30	0 387
Cerotic, liquid	80 to 124	0 607
Lauric, solid	−10 to 25	0 432
Lauric, liquid	40 to 100	0 572
Myristic, solid	−10 to 25	0 405
Myristic, liquid	65 to 142	0 532
Palmitic, solid	−10 to 25	0 484
Palmitic, liquid	65 to 104	0 635
Stearic, solid	0 to 30	0 397
Stearic, liquid	75 to 137	0 550
Valerianic	23 to 93	0.590
Olive Oil (density, 0 911)	6 6°	0 471
Castor Oil .	.	0 434

* Landolt-Bornstein, Tabellen, 768.

(c) Determination of the Chemical Composition of the Fats

(1) **Impurities,** such as water (testing, see page 72), accidental suspended matter, kind and quantity of ash (burning oils should be free from ash or nearly so), should be considered. The presence of nitrogen (*i.e.*, protein matter), of sulphur, of chlorine, etc., is determined as under mineral lubricating oils, see page 77).

(2) **Total Fat.** The total fatty material soluble in ether includes free fatty acids, saponifiable neutral fat, and unsaponifiable oil, the latter being determined according to page 386. The difference between total fat and unsaponifiable matter gives the total saponifiable fat. See page 413. By solution of the fat in a low-boiling petroleum ether

and filtration through a weighed filter it must be remembered that often soaps and oxy-acids or oxidized fats are separated. The soaps are recognized by warming the insoluble matter with petroleum ether and hydrochloric acid, whereby the fatty acids pass into the petroleum ether solution.

In the preparation of curd soaps the glycerine solution may contain salts of oxy-acids which are difficult to salt out; they are not recovered as soap. For this reason Steipel* has worked out the following method for estimating the yield of curd soap from dark-colored soap stock:

A mixture of five grams of fat with 10 c.c. of 50 per cent sodium hydroxide solution and 30 c.c. of alcohol is evaporated to dryness and then heated for 2 hours in a drying-closet at 120°. The soap is decomposed with dilute sulphuric acid and the mass then extracted with petroleum ether. The petroleum-ether extract (free from mineral acid) is then freed from the separated insoluble oxy-acids by filtration into a weighed flask; after the solvent is evaporated, the residue (dried at 100°) is weighed. In this way the fatty acid (free from oxy-acids) plus the unsaponifiable material is obtained, the latter being determined in the usual manner (page 197); from the fatty acids thus obtained is subtracted the amount of free acid (determined as on page 69), the difference being the amount of fatty acid present as neutral fat. From the saponification value (determined by titration with $\frac{N}{1}$ alcoholic potash) the amount of neutral fat is calculated as follows:

If the saponification value of the fatty acid is 198.2 it is possible (by page 401) to calculate the molecular weight (M) of the fatty acid to be 283.1. If the amount of combined acid (a) is found to be 40.2 per cent, the neutral fat may be calculated as follows:

$$x = \frac{a\,(3m + 38)}{3m} = 42.01 \text{ per cent}$$

The total saponifiable fat is the sum of free acid and neutral fat.

If the sample consists of cocoanut oil or palm oil, the residue is not dried after evaporation of the petroleum-ether residue; it is dissolved in alcohol and treated by the method of Hefelman and Steiner (page 406).

The weight represents the total fatty acids (as potassium salts) and unsaponifiable matter; the calculation is carried out as above.

Fahrion,† Davidsohn,‡ and Norman and Hagel§ state that the method is to be used only when the fatty acids are distilled, or are to be made into curd-soap, since the oxy-acids do not distill and their soaps cannot be salted out. In other cases, as in the determination of degras-former (page 413 and 505) the oxy-acids are to be included in the total fat. Soaps from oxy-acids often possess as high lathering power as

* Seifensiedenztg., 40, No. 22 (1913).
† Seifensiederztg., 41, 1150 (1914).
‡ Seifensiederztg., 43, 165, 189 (1916).
§ Seifensiederztg., 43, 456 (1916).

soaps derived from un-oxidized fatty acids; several patents have been issued for the use of oxy-acids.

Goldschmidt and Weiss* state that during the war all refuse fatty material and fatty oils had to undergo a preliminary boiling with spent lyes, so that the impurities might be eliminated and the last traces of glycerine might be recovered; the salts of oxy-acids which dissolved in the lyes were thus lost. Such acids must therefore be separated in the determination of the amount of fatty acid in the fat. As the petroleum ether (B.P. 60°) recommended by Stiepel was difficult to obtain during the war, the above authors extracted the fatty acid (separated by sulphuric acid) with ethyl ether and from the evaporated ether extract the un-oxidized fatty acids were leached with 50 c.c. of boiling petroleum ether (boiling not over 150°).

(3) Essential oils, such as rosemary oil from denaturized olive oil or turpentine from varnishes, are separated by steam distillation from the samples to be examined. Detection of nitrobenzol and nitronaphthalene, see page 75.

Oil of rosemary has a characteristic odor, contains α-pinene, camphene, cineol, camphor and borneol; it has a density of more than 0.9 and a boiling point from 150° to 180°. Lavender oil is yellow or green in color, has a density of 0.88 to 0.89, and is laevo-rotatory. It consists mainly of linalyl acetate and other esters of linalool besides geraniol and cineol, being for the most part saponifiable; it contains no camphor.

(*b*) **Sediments** in oils and fats are often very characteristic and are frequently due to insufficient settling.

1. Sediments may consist of solid glycerides. Fats which are rich in solid glycerides (palmitin, stearin), such as unpressed bone oils and cottonseed oils, deposit at low temperatures (often even at +15°) a part of these. Such deposits are easily melted on gentle heating.

2. Small bits of the seeds, mucilaginous or protein substances which arise from incomplete mechanical purification of the oils, or insufficient settling, are often found in linseed oil, rapeseed oil, etc.

On shaking the oil with an equal volume of warm water, or better, alum solution, a cloudy, white aqueous layer separates, if much mucilaginous matter is present; this cannot be removed by filtration. After long standing, a white, flocculent layer will form between oil and water. (White emulsions may be due to alkali soaps; these, however, are destroyed by adding hydrochloric acid and ether.)

On heating 100 grams of oil to 250° for some time, the mucilaginous and protein-like bodies separate as a flocculent precipitate which can be caught by filtering hot (thus keeping solid glycerides in solution) through a weighed paper; after wash-

* Seifenfabrikant, 37, 579 (1917).

ing off any oil with petroleum ether and drying at 105°, it is examined under a microscope to identify débris of plant cell structures of the various seeds, such as pigment layers, epidermis, hairs, etc. The amount of protein matter in the precipitate can be determined by the Kjeldahl method.

(*c*) **Rosin, Soaps,** etc., are determined as described under lubricating oils on pages 186 and 194.

(*d*) **Testing for Unsaponifiable Substances.** Qualitative tests, see 75; the quantitative determination is carried out according to page 196; the determination of the nature of the unsaponifiable matter separated by the method of Spitz and Hönig is described on page 198.

Natural unsaponifiable materials in fat are often recognized at once to be higher alcohols (cholesterin and phytosterin)*; these are soluble in 90-per cent alcohol (mineral oil is not), from which they crystallize in rhombic plates (cholesterin) or more needle-like forms (phytosterin) (page 399).

Such natural unsaponifiable components of fatty oils have an iodine number of 70 or over; even in the presence of only traces (2 per cent) of mineral oil, which absorbs little iodine, the iodine value is lowered 50 per cent or more.

If the unsaponifiable matter is boiled with twice its volume of acetic anhydride for one hour, on cooling the solution, the mineral oil will collect on the top of the acetic anhydride, the higher alcohols remaining in solution or separating from the liquid as acetates.

(*d*) *Special Tests for the Presence of Certain Oils*

1. **Detection of Peanut (Arachis) Oil.** The presence of arachidic and lignoceric acids, characteristic of peanut oil, allows the detection of additions of ten per cent of this oil.

(*α*) **Preliminary Test.** This depends on the difficult solubility of the potassium salts of arachidic and lignoceric acids in alcohol.

0.7 c.c. of oil are boiled with 5 c.c. of alcoholic potash (33 grams KOH in 1 liter of 90 per cent alcohol) for two minutes, replacing the alcohol which evaporates. In the presence of much peanut oil, the soap solution becomes pasty or gelatinous at room temperature. Additions of 15 per cent peanut oil are detected in olive oils, in poppy-seed oil (at room temperature) and in castor oils (at 0°) by the flocculent precipitate in the alcoholic soap solutions. Tables 95 to 99 give information regarding the external appearance of soap solutions with other oils. Sesame and cottonseed oils give at 20° a strong flocculent precipitate, while rapeseed gives an almost solid mass. Sesame and cottonseed oils are to be detected through their color reactions (page 548), rapeseed oil by its low saponification value.

If the solution has remained clear in the preliminary test, then, in general, the following separation of arachidic acid will be unnecessary.

* Fendler, Ber., d. Pharm. Ges., **1904**, 163.

(β) **Separation of Arachidic and Lignoceric Acids.** According to the amount of peanut oil suspected, 10 to 40 grams of oil are treated, as on page 371, to separate the solid acids, which are then recrystallized from 50 to 100 c.c. of 90 per cent alcohol, in which arachidic and lignoceric acids are much more difficultly soluble than palmitic and stearic acids.* The solutions should not be cooled below +15°. The melting point should then be 70 to 71° (lowered by palmitic and stearic acids); otherwise recrystallization from 90 per cent alcohol should be continued till this melting point is reached. Since, however, at 15°, arachidic and lignoceric acids are soluble in 90 per cent alcohol, allowance must be made for the amount in solution and added to the amount found. The amount of arachidic acid dissolved in 100 c.c. of 90 per cent alcohol at 15° is†

	Grams
with 0.05 to 0.11 gram acid..................	0 033
0.17 to 0.47	0 050
0.50 to 2.70	0.070

These figures have been verified.‡

By multiplication of the weight of acid found by 21, the amount of oil is obtained, since peanut oil contains about one twenty-first of its own weight of arachidic and lignoceric acids.

(γ) According to Fachini and Doria,§ peanut oil is recognized by its content of arachidic acid by dissolving the undried fatty acids precipitated from the soaps (from 20 grams oil) in 150 c.c. of pure acetone (B. P. 56 to 57°), warming gently and then adding water drop by drop till the first sign of cloudiness appears. If the cloudiness persists or two layers appear, then acetone is added till the solution remains clear at 40 to 45°; it is then allowed to crystallize. In the presence of peanut (arachis) oil, at 28 to 29° crystals will appear; after cooling one hour to 15° the crystals are filtered and washed with 10 c.c. of acetone (32 vols. water, 68 vols. acetone). Arachidic and lignoceric acids are then determined by the method of Tortelli and Ruggeri as given above.

(δ) Since pure stearic acid has a melting point of 69.5°, the same as a mixture of arachidic and lignoceric acids, in cases of doubt the molecular weight of the separated acids is determined (stearic 284, arachidic 312, lignoceric 368, mixtures of the last two about 340). If substance sufficient for a molecular weight determination is not available then it is advisable to examine the acids microscopically.|| Stearic acid crystallizes in round frost-like forms, while lignoceric acid gives small needles which form branched structures.

(ϵ) **Special Test for Peanut Oil in Olive Oil.** A simple and rapid method by which as little as 5 per cent of peanut oil may be detected

* Renard, Ztsch. f. anal. Chem., **1873,** 231.
† Tortelli and Ruggeri, Chem. Ztg., **22,** 600 (1898).
‡ Archbutt, Jour. Soc. Chem. Ind., **1898, 1124.**
§ Chem. Ztg. **34,** 994 (1910).
|| Herz, Repert. d. anal. Chem., **6,** 604 (1886).

in olive oil depends on the fact that the crystallization temperature of olive oil fatty acids is lowered in the presence of peanut oil.*

This method of Adler can only be used with mixtures of olive and peanut oils; it would not give correct results if other stearin- or palmitin-rich fats were present.

(ζ) **Detection of Peanut Oil in Ordinary and Hardened Oils.**† 20 grams of oil are saponified by boiling with 10 c.c. of forty per cent sodium hydroxide and 50 c.c. of alcohol, the soap solution is evaporated to dryness and the residue heated with water and HCl in excess till the fatty acids separate clear. After separation in a separatory funnel the fatty acids are dissolved in 100 c.c. (with hardened oils in 200 c.c.) of alcohol and precipitated by adding 1.5 grams of lead acetate in 50 or 100 c.c. of alcohol. After standing from 3 to 15 hours, the separated lead salts are treated with 5 per cent hydrochloric acid; about 2 grams of acids are obtained. They are dissolved in 50 c.c. of 90 per cent alcohol by gentle heating and then cooled 30 min. in water at 15°. The crystals are separated by suction, and again crystallized first from 25 c.c., then from 12.5 c.c. of 90 per cent alcohol. In the presence of 5 per cent peanut oil the melting point of the third crystallization-product will be over 70°. If the separated quantity is small, it is caught on asbestos in an Allihn tube, dissolved in ether and the latter then allowed to evaporate. If the melting point remains under 70°, it may be raised in some cases by recrystallization from another solvent (acetone).

The method of Kreis and Roth gives according to Normann and Hugel‡ products melting over 70° when hardened train or rape oil is tested as the hydrogenization of these oils produces arachidic or behenic acids.

2. **Tests for Crucifer Oils (especially Rapeseed Oil).**

(α) Separation of erucic acid.§ This depends on the fact that erucic acid, which melts at 33 to 34° and has a molecular weight of 338, is more soluble at 0° and at −20° in (96 per cent by volume) alcohol than are the saturated solid acids; and after their separation, the erucic acid is separated with (75 per cent) alcohol, while the greatest amount of liquid acids remains dissolved. The test is made as follows:

25 grams of the acids to be tested are dissolved in two volumes of 95 per cent alcohol and cooled with stirring to − 20° in an ice and rock salt mixture; the precipitate is filtered with suction at − 20° (see Fig. 65, page 109) and washed with cold alcohol. The filtrate is evaporated, dissolved in 75 per cent alcohol and cooled to − 20°. The crystalline precipitate, which in the presence of traces of rape oil, separates in the course of an hour, after filtration with suction and washing with cooled alcohol, appears pure white; it is mostly erucic acid. After solution in warm

* Adler, Zeitsch. f. Nahr. -u. Genussm., **23**, 676 (1912).

† Kreis and Roth, Z. Nahr. -u. Genussm., **25**, 81 (1913).

‡ Chem. Ztg., **37**, 815 (1913).

§ Holde and Marcusson, Ztsch. f. angew. Chem., **23**, 1260 (1910).

benzol or ether, the solvent is evaporated. By titration of a weighed amount of the residue with N/10 alcoholic potash, the acid value, and from this the molecular weight, is determined; in the case of rapeseed oil or similar crucifer oils (mustard oil) this will be over 300 (pure erucic acid 336).

If the original material is very rich in solid fatty acids (train oil), on cooling to $-20°$ the precipitate will be so heavy as to make filtration difficult; in such a case a preliminary cooling to 0° and filtration is advisable, the filtrate being then treated as above.

(β) **Detection of Rape Oil in Olive Oil.** By determination* of the melting point of the most insoluble fatty acids.

The fatty acids from 20 grams of oil, in 100 c.c. of 95 per cent alcohol, are treated with 50 c.c. of a 3 per cent lead acetate solution; the precipitated lead soaps after standing over night are sucked dry, washed 3 times with alcohol, and decomposed by boiling with 5 per cent HCl. The melting point of the solidified fatty acids is determined. This ranges from 50 to 54° for olive oil and 29 to 30° for rape oil, so that an addition of rape oil decreases the melting point, 10 per cent of rape oil giving a value below 50°.

3. **Detection of Tallow and Hardened Fat in Lard.** This depends† on the insoluble glycerides: in lard, alpha-palmito-distearin; in tallow, beta-palmito-distearin. The difference in the melting points of the insoluble glycerides and the fatty acids derived from them is 5.2° with lard, only 0.1° with tallow.

50 grams of fat are dissolved in 50 c.c. ether and allowed to crystallize at 15°; this is repeated, till the melting point of the glyceride is over 61°. The glyceride is then saponified and the melting point of the fatty acids determined. If the fat is soft and rich in olein it should be crystallized from a mixture of 3 to 4 parts ether and 1 part alcohol.

Lard is considered mixed with tallow if the difference (d) between the melting points of the glycerides (G) and of the fatty acids (A) is less than as follows (also if $G + 2\,d$ is less than 71°):

G	61°	61.5°	62°	62.5°	63°	63.5°	64°	64.5°	65°
d	5.0	4.75	4.5	4.25	4.00	3.75	3.5	3.25	3.0

Hardened fats act like tallow in this test; vegetable fats (cocoanut oil, peanut oil, cottonseed oil) do not interfere with the detection of 5 per cent of tallow in lard, while solid vegetable fats (mowrah and shea) are recognized by the phytosterin test.

Cocoanut oil gives 53.3° for $G + 2\,d$; palm nut oil 48.6 to 53.4°;

* Kreis and Roth, Chem. Ztg., **31**, 877 (1913). Z. Nahr. -u. Genussm., **26**, 38 (1913).

† Bömer, Z. Nahr. -u. Genussm., **26**, 559 (1913); **27**, 153 (1914). Also same journal, **27**, 361, 571 (1914); **29**, Heft 17 (1915); **31**, 377 (1916).

cocoanut oil +5 per cent of lard gives 76.3 to 77.3; cocoanut oil with 10 per cent lard, 74.6 to 78.9°; cocoanut oil with 10 per cent of beef tallow gives 66°. With pure butter fat G is over 62.4°, d may be −0.2 to +0.8°; mixtures of butter and lard give higher glyceride melting points, and greater melting point differences.

4. **Testing for Train Oils.** Train oils betray themselves by their pronounced odor and by the red-brown colors given with syrupy phosphoric acid, and with strong alkali; these tests, however, are not always reliable in mixtures of little fish oil and in the presence of oxidized, vegetable drying oils or rancid fats.

(α) More certain is the modified test of Halphen and Lewkowitsch * depending on the fact that the octobromides of fish oils are almost insoluble in boiling benzol, blacken near 180° and are not melted at 230°; hexabromides from linseed oil are soluble in hot benzol and melt near 175°.

Ten c.c. of the fatty acids separated from the oil are brominated by the Halphen method by shaking in a glass-stoppered measuring cylinder with 200 c.c. of a mixture of 20 vols. glacial acetic acid, 4 vols. nitrobenzol and 1 vol. of bromine. If no precipitate forms in the course of an hour the sample is practically free from fish oil or oil containing linolic acid. The yellow precipitate which does form is sucked dry on a filter plate and washed with ether till white. To determine if it contains octobromide, after drying and powdering, two grams are boiled with 100 c.c. of benzol for ½ hour under a reflux condenser; the undissolved material is collected on a hot-water funnel and after drying, its melting point is determined; if it is not melted at 200° but is blackened due to decomposition, fish oil is present. If a melting point under 200° is found, an attempt should be made to raise the melting point by leaching with benzol. The hexabromides of the drying vegetable oils melt at 175 to 180° without decomposition. Ten per cent of fish oil can be detected by this method.

Not only the fatty acids from fish oils but the fish oils themselves give, in the presence of the Halphen reagent, difficultly soluble bromides. In case, therefore, that oils and not soaps are to be tested for fish oils, the oils may be directly treated with bromine solution; if no precipitate results, fish oils are absent. If a precipitate forms the total fatty acid should be separated and brominated as above.

This test, according to Stiepel,† is not applicable if the products have been heated; with linseed oil the amount of hexabromide formed becomes considerably less; with fish oils the yield of octobromide may become zero (see also page 414).

Marcusson and Böttger‡ found that clupanodonic acid, upon which the above test depends, occurs not only in train oil but also to a

* Marcusson and Huber, Seifensiederzeitung, **38**, 249 (1911).

† Seifensiederztg., **39**, 953 (1912).

‡ Chem. Ztg., **39**, 14 (1915); also **40**, 244 (1916). Seifensiederztg., **42**, Nr. 32 (1915). Seifenfabrikant, **35**, 253 (1915).

small extent in bone oils and lard oils which yield from 0.25 to 1 per cent of octobromide against 10 to 34 per cent with train oils. If more than 1 per cent of octobromide is found an adulteration with train oil may be suspected. In cases of doubt the inner iodine value (page 374) may be used, as for land animals, this will be under 100, for marine animals over 100.

(β) **Reaction of Tortelli and Joffe.*** This allows the detection of heated, and hardened, train oil. (Page 439.)

Some of the oil is carefully dried and treated one hour at 100 to 120° with fuller's earth; 1 c.c. of this oil is dissolved in a glass-stoppered cylinder in 6 c.c. of chloroform and 1 c.c. of glacial acetic acid and then quickly mixed with 40 drops of 10 per cent bromine solution (in chloroform). (With hardened train oil, 5 c.c., in the melted condition, is dissolved in 10 c.c. of chloroform and 1.5 c.c. of glacial acetic acid, and then 2.5 c.c. of bromine solution added). Vegetable fats and oils give a yellow to reddish-yellow color. Train oils take on a rose color; a green color develops after from 5 min. to 1 hour

This reaction has given satisfactory results with deodorized train oils (but not old menhaden or sardine oils). Only when oils are almost completely hydrogenated will the test fail. Others have had difficulty with this test.

5. **Test for Tung Oil.**† In treating china wood oil with iodine a portion solidifies and becomes insoluble in petroleum ether; the amount of oil remaining soluble is used to estimate the amount of other oil present.

Five grams of oil are warmed with 10 c.c. of glacial acetic acid and to the clear solution are added 50 c.c. of a solution of 1.5 per cent iodine in glacial acetic acid. After a half hour the flask is drained into a separatory funnel, the residue being washed with 50 c.c. portions of petroleum ether to separate all oily portions, these washings being added to that portion in the separatory funnel. The ether layer is washed free from acid with water, then free from iodine with potassium iodide solution and then again with water. After evaporating the petroleum ether, the residue is weighed; china wood oil gives no soluble residue.

6. **Color Reactions for Sesame and Cottonseed Oils.** Of the large number suggested, the following appear to be the best:

(α) **The Baudouin Test,** a cherry red color developed by sesame oil in the presence of hydrochloric acid solution containing sugar, is given sharply by 1 per cent sesame oil in other oils, while 0.5 per cent is still recognizable by a faint rose colored solution; pure olive, rape and hemp-seed oils only give a yellow color to the acid.

* Chem. Ztg., **39,** 14 (1915).

† McIlheny, Jour. of Ind. and Eng. Chem., **4,** 496 (1912).

0.1 gram cane-sugar is dissolved in 10 c.c. of hydrochloric acid (sp. gr. 1.19) and then shaken with 20 c.c. of oil in a test tube and allowed to stand. Only the color developed immediately after separation of the layers should be considered, since on long standing, the acid sugar solution will of itself become deep brown or red brown in color. The substance* causing the reaction is said to be a thick alcohol-soluble oil.

Villavecchia and Fabris† state that the acid forms furfurol from the sugar and suggest the following modification:

Five c.c. of oil and 5 c.c. of hydrochloric acid (sp. gr. 1.19) are shaken with 8 drops of a two per cent alcoholic solution of furfurol for ½ minute in a test tube. In the presence of sesame oil (1 per cent) the separating acid takes on a carmine red color; in the absence of sesame oil, the color becomes at most yellow or brownish yellow. Here also the color must be observed immediately after making the test

Since a small addition of sesame oil is easily detected, the addition of at least 10 per cent of sesame oil to margarine is required‡ in Germany to distinguish it from butter. The sesame oil added, when mixed with cottonseed or peanut oil in the proportion of 0.5 to 99.5, should still give a decided furfurol reaction. According to recent investigations§ the substance responsible for the furfurol reaction passes, in certain cases where cows have been fed with sesame press cakes, into the milk and therefore appears in the butter; for this reason pure butter may give the sesame oil reaction. In case of doubt, the phytosterin acetate test is also to be used (page 399).

According to Soltsien, from 10 to 20 per cent of sesame oil cannot be detected in older fats; after eight weeks the reaction is no stronger than with a fresh 1 per cent of sesame oil.|| If the oil has been treated with animal charcoal the reaction fails also.¶

In making this test it must be remembered that coal-tar colors are added to many fats and oils; these give a red color when hydrochloric acid is added. The substances causing the appearance of the red color should be leached out previously by successive treatments with hydrochloric acid of specific gravity 1.125. This leaching may, however, cause an error in that the substance** which is the cause of the

* Merkling, Arch. d. Pharm., **10**, 440.

† Ztsch. f. angew. Chem., **6**, 505 (1893).

‡ Ausführungsbestimmungen zum Gesetz, betr. Verkehr mit Butter und Käse, om 15, Juni 1897.

§ Utz, (Ubbelohde, Handbuch, Bd. I, 279).

|| Zeitsch. f. öffentl. Chem., **1899**, 15.

¶ Bömer, Ztsch. f. Nahr. u. Genussmit., **1899**, 708.

** Soltsien, Zeitsch. f. öffentl. Chem., **1897**, 494; Siegfeld, Milchzeitung, **1899**, 243; Fendler, Chem. Rev., **12**, 10 (1905).

furfurol reaction may also be leached out with the coloring material; for this reason the Soltsien reaction is preferable with colored fats.

(β) **The Soltsien Reaction for Sesame Oil.** This is highly recommended * since it can be used even in the presence of coal-tar colors, these being reduced to colorless bodies by the stannous chloride.

3 volumes of oil or fat (melted, if necessary, on a water bath) are dissolved in twice this volume of naphtha (boiling limits, 70 to 80°) and then shaken with 3 volumes of a hydrochloric acid solution of stannous chloride (Bettendorf's reagent, prepared by saturating a concentrated solution of stannous chloride with dry hydrogen chloride gas) and then dipped in a water bath at 40°. After the separation of the tin solution, the test tube is lowered in water at 80° up to the level of the tin layer, thus preventing as much as possible evaporation of naphtha. In the presence of sesame oil the tin chloride solution becomes red in color.

Soltsien states that the substance causing this reaction cannot be extracted from the oil with hydrochloric acid † since the extracted oil gives the color with undiminished intensity.

(γ) **The Halphen Test for Cottonseed Oil.** ‡

Two c.c. each of oil, amyl alcohol and a 1 per cent solution of sulphur in carbon disulphide are heated in a test tube half immersed in a boiling salt solution (see Fig. 126). The distilled carbon disulphide collects in the lower vessel. If after 10 minutes boiling a red or orange color has not appeared, fresh solvent is put in place of that evaporated and the heating continued for 10 minutes. Five per cent of cottonseed oil can be detected by the appearance of the red color in the amyl alcohol solution; the reaction is not given by olive, rape, hempseed, almond, peanut, sesame, poppy-seed and fish oils. Fish oils on repeated heating do show a faint coloration; but by moving the tube so that the oil runs down the side of the tube the red color cannot be seen in that portion draining down the sides; on the other hand oils containing small amounts of cotton oil show a red color even on draining down the sides of the tube. The color varies from orange to deep red.

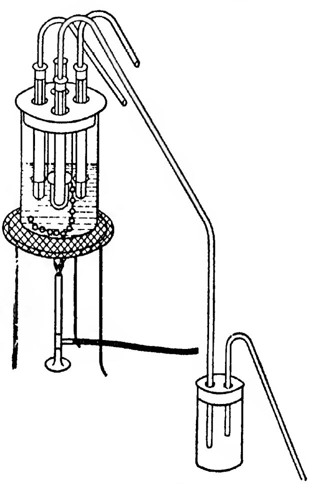


FIG. 126.

The reaction is made still sharper§ if 4 c.c. of oil and 4 c.c. of sulphur

* Beythien, Chem. Ztg., **24**, 1019 (1909); Utz, Chem. Ztg., **25**, 412 (1901).

† Chem. Rev., **13**, 138 (1906).

‡ Journ. Pharm. Chim., [6] **6**, 390; Chem. Zentralbl., **1897**, II, 1161.

§ Chem. Umschau., **20**, 89 (1913).

in carbon disulphide are heated with a few drops of pyridine for 10 to 30 minutes; in this way 0.25 per cent of cottonseed oil may be detected.

The Halphen test is said to be given by kapok oil about 15 to 20 times as intensely as by cottonseed oil (Besson). To distinguish between these oils Milliau suggests dissolving the oil in chloroform and adding 2 per cent alcoholic silver nitrate solution. Cottonseed oil gives an intense yellow color; kapok oil gives a coffee-brown, quickly developing color.

The Halphen reaction is given by oils which have been heated up to 210°, but is not given after a 10 minute heating to 250°; nor is it given by blown oils or oils treated with fuming hydrochloric acid or with chlorine or sulphurous acid. The oil shaken with hydrochloric acid* has a lower iodine value than the original and gives a chlorine test with copper, from which it may be inferred that the substance giving the Halphen reaction is an ethylene or acetylene derivative; Raikow† had previously assumed the substance to be an unsaturated acid. The red color is said to arise by the addition of sulphur to the double or triple bond with the formation of a chromophoric sulpho-aldehyde- or sulpho-keto-group. The intensity is not the same for the different samples of cottonseed oil; the colors vary from orange to deep red. The color-giving substance appears to be present only in very small quantities and appears also to be retained to a certain extent in the press cakes; if swine are fed with these, this substance appears to become a part of the body fat of the animal. The Halphen reaction is therefore given by some fats which contain no cottonseed oil; in this case the presence of cottonseed oil must be tested for by the phytosterin acetate method (see page 399).

(δ) In case the Halphen test is not given and the presence of cottonseed oil is suspected, it can sometimes be detected by treatment with strong nitric acid.

On shaking cottonseed oil with the same volume of nitric acid (sp. gr. 1.41), a red-brown color will appear, while olive oil treated in the same manner will give a dirty yellow color which on long standing will pass over into brown. Twenty per cent of cottonseed oil in olive oil can be detected by this method; since, however, on shaking rape oil with nitric acid, a brown color appears, the reaction has value only as a preliminary test for large additions of cottonseed oil.

(ϵ) **The Silver Nitrate Test‡** depends on the reduction of silver nitrate by an aldehyde-like body, as yet unidentified, present in cottonseed oil.

* Kühn and Benger, Ztschr. f. Nahr. -u. Genussm., **12,** 145 (1906).

† Chem. Ztg., **24,** 584 (1900).

‡ Milliau, Comp. Rend., **1888,** 550.

Five c.c. of the fatty acids separated from the oil are dissolved in 15 c.c. of 90 per cent alcohol and heated 1 to 3 minutes with 2 c.c. of a 3 per cent aqueous silver nitrate solution; in the presence of cottonseed oil the liquid will darken in color and the fatty acids, colored dark by the metallic silver, will rise to the surface.

Five per cent of cottonseed oil gives a sharp test, while 1 per cent is still recognizable by a chocolate brown color; strongly heated oils give a fainter test or none at all.

7. **Other Color Reactions.**

According to Holde, raw mustard oil, linseed and hemp-seed oils on shaking with sulphuric acid of specific gravity 1.53 to 1.62 always give an intense grass-green to bluish-green coloration; refined rape and linseed oils give with sulphuric acid of specific gravity 1.62 only a faint yellow to brown color. This test can therefore be used to distinguish between raw and refined rape or linseed oils.

8. **A Test for Vegetable Fats has been suggested by Serger.***

The reagent is prepared shortly before use by shaking 10 c.c. of conc. sulphuric acid with 0.1 gram of finely powdered sodium molybdate for 2 minutes; it is ready for use after standing five minutes, but should not be kept longer than ½ to 1 hour. Five c.c. of the oil are dissolved in 10 c.c. ether in a thick-walled glass-stoppered graduated cylinder and 1 c.c. of the reagent is carefully run underneath; after short but vigorous shaking two layers will separate, the lower one assuming a characteristic coloration which increases in intensity. The color is judged after 15 minutes. Sesame oil† takes on an olive green color, which later becomes darker; olive oil a faint yellowish green; cocoanut oil gives a grass green color; while cottonseed oil gives a blue-green, then dark blue. The test may fail if bleached or rancid fats are under examination. Ten per cent of vegetable oil can be detected by this method.

9. **Cocoanut Oil** also gives a color reaction‡ which depends on a reaction of lauric acid, which is one of the main constituents of cocoanut oil, with furfuramide. Oleic acid, one of the most important components of butter and lard, unites with the furanilide, which is the cause of the color, and hinders the formation of the color.

One-half a gram of aniline hydrochloride dissolved in 25 c.c. of 96 per cent alcohol is mixed with 5 c.c. of a 1 per cent alcoholic furfurol solution and 1 c.c. of phenol, and to the faintly red mixture 5 per cent ammonia solution is added drop by drop till the red color disappears or changes to a yellowish red.

After standing for two hours, 0.5 c.c. of this reagent is added to a solution of 20 drops of the acids to be tested (in 5 c.c. of 96 per cent alcohol), the upper part of the test tube not being wet by the reagent. The mixture is then shaken once and allowed to stand; with lauric and other acids of low molecular weight a red color appears, with oleic acid a yellow color. If to the red solution 10 drops of oleic acid are added, it changes to yellow.

10. **Test for Castor Oil.** Castor oil differs from other fatty oils

* Chem. Ztg., **35**, 581 (1911).

† Utz, Chem. Rev., **19**, 72 (1912)

‡ Zeitsch. f. Nahr. -u. Genussm., **13**, 605 (1907).

and liquid waxes in being soluble in concentrated alcohol but insoluble in naphtha or petroleum ether. The ricinoleic acids are insoluble in petroleum ether though they may dissolve if 90 per cent of oleic acid is present. On fusion of castor oil with potash there forms octyl alcohol with characteristic odor, and sebacic acid $C_{10}H_{18}O_4$. The latter is recognized by dissolving the fusion mixture in water, adding magnesium chloride to precipitate other acids; after filtration, the filtrate is acidified and the free-acid allowed to crystallize.

When castor oil is distilled in a vacuum n-heptylaldehyde $C_7H_{14}O$, acrolein, and other bodies form.

11. **Biologic Test for Fats.** This depends on the fact that the blood serum of a rabbit treated with the serum of another animal, for example, a horse, causes a precipitation of protein matter in the serum of the latter. In order to detect the presence of, say, horse fat in other fats by means of this reaction* 50 grams of fat are leached with 200 c.c. of 0.85 per cent sodium chloride solution in a sterile Erlenmeyer flask, by placing for two hours in a freezing mixture and shaking frequently; with the salt solution poured off, a second 50 gram portion of fat is leached, so that the protein content rises to 0.3 per cent. The protein solution, clarified by twice filtering through diatomaceous earth, is placed as a layer beneath some serum of a rabbit previously treated with horse serum; after a few minutes, in the presence of horse fat in the original sample, a cloudiness in the form of a distinct ring will develop.

Popoff and Konsuloff† tested selected plants (not hybrids) by pressing below 65° (or by extraction) so that protein remained in the oils. By immunizing rabbits (intra-peritoneal injection) with extracts from peanuts and sesame seeds in physiological salt solution there were obtained specific sera by means of which additions of peanut oil or sesame oil to olive oil could be detected.

(e) *Differentiation of Vegetable and Animal Fats*

The vegetable fats may be distinguished from animal fats by means of the phytosterin‡ test. Cholesterin acetate melts at 114.3 to 114.8 (corrected) while phytosterin melts between 125.6 and 137° (corrected). Phytosterin acetate is more difficultly soluble in alcohol than is cholesterin

* Uhlenhuth und Weidanz, Praktische Anleitung zur Ausführung des biologischen Eiweissdifferenzierungsverfahrens, Jena, 1909; Wittels and Welwart, Seifersiederztg., **37,** 1014 (1910).

† Z. Nahr. -u. Genussm., **32,** 123 (1916).

‡ Bömer, Z. Nahr. -u. Genussm., **1901,** 1070.

acetate, so that by recrystallization from alcohol the phytosterin acetate collects in the separating crystals.

The free sterins are separated with digitonin by the method of Windaus.* Fifty grams of oil or fat in a separatory funnel are shaken 15 minutes with 20 c.c. of a one per cent solution of digitonin in 96 per cent alcohol. After standing some hours, the clear separated oil is run off as completely as possible; the flocculent precipitate in the alcohol layer is extracted with 50 to 100 c.c. of ether, the precipitate collected and washed free from oil by means of ether. Solid fats must be shaken at a temperature of 70° or treated in the presence of a solvent like benzol or chloroform.

The above method has been modified†: The fat with the digitonin solution is stirred 5 minutes at 60 to 70° by means of a turbine, then diluted with benzol and chloroform and the sterin precipitate filtered. By this modification, it has been possible to detect 5 per cent (as low as 1 per cent) of vegetable fat in animal fat. It does not appear to be necessary to saponify before precipitating with digitonin; the amounts of free sterins present in vegetable fats appear to be sufficient for the detection of the phytosterin.

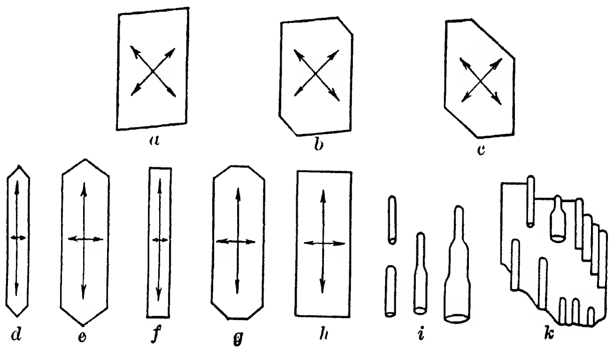


FIG. 127.

The air-dried digitonid is powdered and extracted with ether, then the digitonin separated‡ by heating with 1.5 c.c. of acetic anhydride for 30 minutes. The separating acetates are recrystallized from alcohol and the melting point determined. If this remains constant at 115°, the fat was purely animal in origin; if it is higher, vegetable oil was present. The sterins can be re-obtained from the acetates by saponification; on separation and microscopic examination, cholesterin will show the form of (*a*) in Fig. 127, less frequently (*b*) and (*c*),

* Chem. Ztg., **37**, 1001 (1913).

† Fritzsche, Z. Nahr. -u. Genussm., **26**, 644 (1913). Also **27**, 713 (1914); **28**, 129, 138 (1914).

‡ Windaus, Ber., **42**, 244 (1909). Also Z. physiolog. Chem., **106**, 1 (1917).

while phytosterin will show the forms (*d*) and (*e*), less often (*f*), (*g*), and (*h*).

The detection of animal in vegetable oil can only be accomplished when large amounts of the former are present; as a matter of fact vegetable oil is rarely adulterated with animal oil because of the difference in price, so that the problem of detecting it rarely arises. With the cheap fish oils the high cholesterin content (see also page 392) allows the detection of small additions; and for the so-called liquid waxes, such as sperm oil, dolphin oil, their low specific gravity, their low saponification value, etc., serve for identification.

(*f*) *Quantitative Constants of Fats*

1. **The Acid Value** is determined as in the case of mineral oils (see page 69). If the fat is solid so that it is impossible to take 10 c.c., about 5 grams of substance should be weighed and titrated in neutral benzol-alcohol solution with $\frac{N}{10}$ potash. In the presence of ammonium, alkaline earth or metallic soaps, the method of page 227 is used (alkali soaps do not interfere).

2. **The Saponification (Köttstorfer) Value.** The saponification value is the number of milligrams of KOH required to saponify one gram of fat. As may be seen from Tables 95 to 101, rape oil, mustard oil, castor oil and sperm oil are characterized by their low saponification values as compared with the other fats; mixtures containing mineral oil show a low value, which may be used in determining the amount of mineral oil (see page 196).

(*α*) **Method of Köttstorfer.***

1.5 to 2 grams of oil are boiled in an Erlenmeyer flask (Jena glass†) of 200 c.c. capacity for 15 minutes under a reflux condenser with 25 c.c. of $\frac{N}{2}$ alcoholic potash measured from a pipette; a blank test with 25 c.c. of the solution is run simultaneously, every operation being exactly the same as with the sample. The blank test is necessary in view of changes of temperature and the solubility of the glass in alkali. After saponification, 50 c.c. of neutralized alcohol are added to the sample and then titrated back with $\frac{N}{2}$ hydrochloric acid in the presence of phenolphthalein; the amount of acid necessary to neutralize the 25 c.c. is also determined.

Example: 2.2334 grams oil are saponified with 25 c.c. of alkali. 25 c.c. of alkali neutralize 23.36 c.c. of $\frac{N}{2}$ acid; 8.00 c.c. of acid were required to titrate back the excess. The alkali used was therefore equivalent to 15.36 c.c. of acid; but

* Ztsch. f. anal. Chem., **18,** 199 (1879).

† Hefelmann und Mann, Pharm. Zentralhalle, 1895.

1 c.c. of $\frac{N}{2}$ HCl neutralizes 0.028 gram of KOH, consequently 15.36 c.c. will neutralize 0.43008 gram KOH. This 0.43008 gram was required by 2.2334 grams of oil, or 1 gram required 192.6 milligrams of KOH to saponify and 192.6 is taken as the saponification value.

With mixtures of mineral oils, proceed as on page 197. Fish oils give a dark red solution with alcoholic potash which makes titration with phenolphthalein difficult; in such cases use alkali blue (Höchst), red in alkaline, blue in acid solution. For titration of the soap 3 c.c. (2 c.c. for the blank test) of a 2 per cent alcoholic solution of the indicator should be used.

For the saponification of waxes see page 519 and 523.

(β) **The Cold Process of Henriques*** depends on the fact that saponifiable glycerides, as well as beeswax, insect wax, etc., dissolved in petroleum ether or naphtha, will be completely saponified in 18 to 20 hours on the addition of normal alcoholic potash; the method can be used when time is not lacking, but up to the present has found comparatively little application. For mixtures of mineral oils with fatty oils and for wool fat the hot saponification should always be used

3 to 4 grams oil are dissolved in an Erlenmeyer flask in 25 c.c. petroleum ether (beeswax and insect wax in naphtha boiling at 100°) and then 25 c.c. of $\frac{N}{1}$ alcoholic potassium hydroxide, which should contain not more than 3 per cent of water, are added. A blank test is run at the same time. Both flasks should be kept closed with an elastic rubber cap. After standing over night, the contents of both flasks are titrated with $\frac{N}{2}$ acid as in (α).

Those oils which have a high saponification value (porpoise oil, 216 to 272, palm nut oil, 248, cocoanut oil, 246 to 268) contain considerable amounts of volatile acids with low molecular weight, which is also made evident by the Reichert value 2.5 to 65. See Tables 95 and 101.

3. **Average Molecular Weight of the Fatty Acids.** In order to determine in a mixture of saponifiable and unsaponifiable oil the nature of the former, there should be determined, besides the iodine value, the average molecular weight of the fatty acids; this is also of importance in the calculation of the amount of soap (page 195).

This was formerly done by dissolving 0.5 to 1 gram of the fatty acid in neutralized alcohol and titrating with $\frac{N}{10}$ alkali; from the

* Ztsch. für. angew. Chem., 4, 721 (1891).

neutralization value thus determined, the molecular weight was calculated. By this method, however, too high* values were obtained, since the acids separated from the fats contained anhydride or lactone-like bodies which were not attacked by the cold alkali; the amount of such bodies is greater in old oils.

To determine the true molecular weight 1 to 2 grams of the fat are to be boiled with 25 c.c. of $\frac{N}{2}$ alcoholic potash and then titrated back with $\frac{N}{2}$ acid. A blank test should be made. The saponification value is then calculated. The molecular weight is obtained as follows:

$$M = \frac{56,110}{S},$$

where S is the saponification value, M is the molecular weight and 56,110 is the number of milligrams in one gram-molecular weight of KOH.

Tortelli and Pergami found the differences between the neutralization and the saponification values to range from 0 to 20; for rape oil, for example, it was, according to age, 5.7 to 9.1; for cottonseed oil, 3 to 14.4; for linseed oil, 10.3 to 19.6. The average molecular weights of the insoluble fatty acids of several fats and oils are given in Table 91.

TABLE 91

AVERAGE MOLECULAR WEIGHTS OF FATTY ACIDS

	Tortelli and Pergami	Material-prufungsamt
Almond oil	277.5	267.4
Cottonseed	274.3	262.6
Peanut	280.5	..
Colza (rape)	309.1	303.6
Castor	296.7	...
Linseed	273.2	275.3
Olive	279.1	...
Beef tallow	270.8	...
Lard	276.2	...
Vegetable tallow	262.1	...
Bone oil	...	273.2

The following table (92) gives the molecular weights and saponification values of a number of pure triglycerides; of these the last eight in the table are found in lubricating oils.

* Tortelli and Pergami, Chem. Rev., 9, 182, 204 (1902).

TABLE 92

Triglyceride	Formula	Molecular weight	Saponification val.
Butyrin..	$C_3H_5(O \cdot C_4H_7O)_3$	302	557.3
Valerin	$C_3H_5(O \cdot C_5H_9O)_3$	344	489 2
Caproin	$C_3H_5(O \cdot C_6H_{11}O)_3$	386	436 1
Caprin .	$C_3H_5(O \cdot C_{10}H_{19}O)_3$	554	303 7
Laurin	$C_3H_5(O \cdot C_{12}H_{23}O)_3$	638	263 8
Myristin.	$C_3H_5(O \cdot C_{14}H_{27}O)_3$	722	233 1
Palmatin	$C_3H_5(O \cdot C_{16}H_{31}O)_3$	806	208 8
Stearin ..	$C_3H_5(O \cdot C_{18}H_{35}O)_3$	890	189.1
Olein	$C_3H_5(O \cdot C_{18}H_{33}O)_3$	884	190 4
Linolein	$C_3H_5(O \cdot C_{18}H_{31}O)_3$	878	191.7
Ricinolein	$C_3H_5(O \cdot C_{18}H_{33}O_2)_3$	932	180.6
Erucin	$C_3H_5(O \cdot C_{22}H_{41}O)_3$	1052	160.0

4. **The Ester Value.** This gives the number of milligrams of KOH necessary to saponify 1 gram of the neutral fat; the saponification value may be considered as the sum of the acid value and the ester value. The ester value is determined either by difference or directly.

In the latter case 2 grams of fat are neutralized with $\frac{N}{10}$ alcoholic NaOH in neutral benzol-alcohol solution, the solvent is evaporated and the residue boiled under a reflux condenser with 25 c.c. of alcoholic $\frac{N}{2}$ KOH for 15 minutes; the excess is then determined as usual with $\frac{N}{2}$ acid (see page 69).

The determination of the ester value is rarely made with lubricants. The ester value is, however, of importance in the examination of beeswax for which the ratio of the acid value to the ester value is characteristic (see page 523).

5. **The Reichert-Meissl and the Polenske Values.** The per cent of volatile acid contained in a fat is generally not determined. But comparative values of the amount of volatile acids contained are determined by the Reichert-Meissl method which measures the saturation capacity of the volatile fatty acids contained in a definite amount of fat.

The Reichert-Meissl value is the number of c.c. of $\frac{N}{10}$ potash necessary to neutralize the volatile water-soluble acids obtained from 5 grams of fat by the method described below. The Reichert-Meissl value is determined in lubricating oils only when the saponification value is noticeably large, which is caused by the presence of porpoise oil, palm nut oil or blown oils. It is used mainly to detect adulterations

of natural butter with margarines, lard and cocoanut oil; margarines and lard contain very small amounts of volatile acids with Reichert-Meissl value 0 to 1, while cocoanut oil has the values 5 to 8. These additions therefore decidedly lower the Reichert-Meissl value of natural butter which lies between 20 and 30; small amounts of cocoanut oil are, however, hard to detect by this method. This can be done with the help of the Polenske value, which gives the number of c.c. of $\frac{N}{10}$ alkali necessary to neutralize the volatile, water-insoluble acids in 5 grams of fat.

The ratio of the volatile water-insoluble fatty acids to the volatile soluble acids is large in the case of cocoanut oil and small in the case of butter.*

TABLE 93

	Reichert-Meissl value	Polenske value	$\left(\frac{\text{Polenske}}{\text{Reich.-Meissl}}\right)100$
Butter....................	26 to 33	1 9 to 3 0	7 3 to 9.1
Cocoanut oil................	5 to 8	16 8 to 17 8	223 to 336

The determination of these values is carried out as follows:†

(α) **Reichert-Meissl Value.** To succeed with this method, the directions must be carefully followed and the dimensions of the apparatus should not be different from those given in the sketch (for example the flask should not be larger than 300 c.c., otherwise the results will come out too high).

Five grams of filtered butter fat are saponified‡ with 20 grams of glycerine and 2 c.c. of sodium hydroxide solution containing 100 grams NaOH in 100 c.c. water in a 300 c.c. Erlenmeyer flask, agitating constantly over a free flame until the liquid becomes clear. The soap is dissolved in 90 c.c. of boiled water; the solution should be clear and almost colorless. To the soap solution, heated to 50°, at first are added 50 c.c. of dilute sulphuric acid (25 c.c. of conc. acid to 1 liter water) and then a small amount of powdered pumice-stone, and immediately after closing the flask distillation is begun in the apparatus shown in Fig. 128. The use of an iron wire gauze under the flask is to be avoided; best adapted for this purpose are the flat asbestos plates of 6.5 cm. diameter, but neither the plate nor the iron ring supporting it should be heated to the glowing point. The distillation should be carried

* Benedikt-Ulzer, 5th Edition, 973.

† Ztsch. f. Nahr. -u. Genussm., **1904**, 273.

‡ Leffmann and Beam, Analysis of Milk and Milk Products, Philadelphia, **1893**, 65.

on with fully opened burner, using, however, only the tip of the flame, since overheating gives incorrect, generally too high results.

The 110 c.c. distillate should pass in 19 to 21 minutes and should have a temperature about 20° as it drops from the condenser. As soon as the distillate reaches the 110 c.c. mark the flame is withdrawn and the receiver is replaced by a 25 c.c. graduated cylinder.

The flask and distillate, without previously mixing the contents, is placed for 10 minutes in water at 15°, the mark 110 being about 3 cm. under the surface of the water; after 5 minutes the flask is so agitated that the acids floating on the surface of the distillate will reach the walls of the neck; after 10 minutes, the state of aggregation of the acids is determined (with pure butter, semi-solid and opaque; with cocoanut oil, oily). After stoppering, the distillate is mixed by inverting the flask repeatedly, avoiding too violent agitation, and is then filtered through a smooth 8 cm. filter. 100 c.c. of the filtrate are then titrated with $\frac{N}{10}$ sodium hydroxide in presence of phenolphthalein. The number of c c. of alkali, multiplied by 1.1 (of 110 c.c. distillate only 100 were used for titration) gives the Reichert-Meissl value.

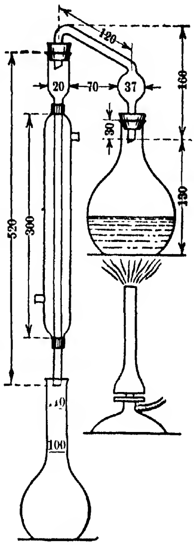


FIG. 128.

(β) **Polenske Value.** To determine the water-insoluble volatile acids, a complete removal of water-soluble acids is necessary. The filter paper used above is washed with three 15 c.c. portions of water which have previously passed through the condenser tube, the graduated cylinder placed beneath it and through the 110 c.c. flask; then three 15 c.c. portions of neutral alcohol (90 per cent) are passed through in the same way. The combined alcoholic filtrates are then titrated with $\frac{N}{10}$ sodium hydroxide. The number of c.c. used gives the Polenske value. The variations should not be more than 10 per cent with values up to 2; 8 per cent, from 2 to 5; 5 per cent, from 5 to 10; and 4 per cent, from the value 10 on.

(γ) In mixtures of fatty oil with mineral oil (for example, "marine oil"), mixtures of mineral oil with blown rape oil or cottonseed oil, see page 500) the Reichert-Meissl value is determined as follows:*

As much of the mixture as corresponds to 5 grams of fatty oil is saponified with normal alcoholic potash, in the presence of the same volume of benzol, the unsaponifiable material separated by the method of Spitz and Hönig (page 197), the alcohol evaporated from the soap solution and the residual soap solution treated as above. A blank test with a mixture of benzol and alcoholic potash should be made at the same time. The values obtained are referred to the amount of fatty oil contained in the sample.

* Marcusson, Mitt., 23, 45 (1905).

6. **The Hehner Value** gives the per cent of water-insoluble fatty acids in the fat; this is of value in determining the worth of raw materials in the stearic acid industry, and in the examination of soaps.

The customary method of determining this value, in which a weighed amount of fat is saponified, the acids liberated with mineral acid, filtered, washed with water, dissolved in alcohol, the alcohol evaporated and the residue weighed, has, besides neglecting the water-soluble acids, the disadvantage of favoring the oxidation of unsaturated acids during the evaporation and also of allowing loss of volatile portions. See page 469.

More exact results are given by the method depending on the weighing of the alkali salts of the fatty acids;* in this method also, the solubility of acids in water is neglected.

7 to 8 grams of the soaps are dissolved in 50 c.c. of water and then treated with 40 c.c. of 10 per cent sulphuric acid in a separatory funnel; the fatty acids are then extracted by shaking twice with 50 c.c. portions of ether and the extract washed three times with 10 c.c. portions of water to remove mineral acid. The ether solution is then put into a 300 c.c. Phillips flask (Erlenmeyer with wide mouth) which has previously been weighed with some ignited coarse sand and a stirring rod. About half the ether is evaporated, then 50 c.c. of neutral alcohol are added and the acids titrated with carbonate-free $\frac{N}{1}$ alcoholic potassium hydroxide with phenolphthalein as an indicator; the soap solution is then evaporated to dryness with stirring on a water bath and the residue is heated to constant weight at 103 to 105°, the mass being stirred occasionally with the rod. Drying at a higher temperature is apt to cause decomposition. The fatty acid is calculated as follows:

$$x = s - (0.03814)\,(v),$$

where s is the amount of alkali salt weighed, while v is the number of c.c. of $\frac{N}{1}$ potash used.

The majority of fats have a Hehner value of 92 to 95, generally 95. The Hehner value is naturally lower in those fats which have high Reichert-Meissl values. The Hehner values of some fats are given:

Cocoanut oil	83.8 to 90.5
Butter	86 to 88
Palm nut oil	87.6 to 91.1
Dolphin oil (from the head)	66.3

7. **Iodine Value.** By iodine value is meant the number of grams of halogen, calculated as grams of iodine, which are absorbed by 100

* Ztsch. f. angew. Chem., **22**, 255 (1909).

grams of fat under definite conditions (time of contact, nature of the iodine carrier, excess of iodine, etc.).

The iodine value is one of the most important criteria in the testing of the purity of a fat (Tables 95 to 101). According to the size of the iodine value, the fats are divided into drying oils with iodine values from 130 to 200 (linseed oil, wood oil, poppy-seed oil), semi-drying oils with iodine values ranging from 95 to 130 (corn oil, rape oil, cottonseed oil, sesame oil) and non-drying oils with iodine values under 95 (olive oil, peanut and castor oils). The iodine values of fats of land animals are under 80, those of marine animals generally over 100.

Iodine is very slow in its action on fats at ordinary temperatures, while at higher temperatures its action is variable and it does not act smoothly. On the other hand, according to Hübl, an alcoholic iodine solution in the presence of mercuric chloride reacts quantitatively with fatty acids and their glycerides at ordinary temperature. The reaction goes on essentially with the addition of iodine chloride* which forms, according to Ephraim and Wijs, by the reaction:

$$HgCl_2 + 2\ I_2 \rightarrow HgI_2 + 2\ ICl.$$

The amount of iodine added corresponds to two atoms of halogen in the case of acids with one double bond, four atoms in the case of linoleic acid and six atoms in the case of linolenic acids; it is thus decidedly higher in the case of the drying oils than with non-drying oils.

Complete absorption with the Hübl or Waller iodine solutions is obtained with 50 per cent excess only after 18 to 24 hours' contact, while 2 hours' contact is required with 75 per cent excess.

It is claimed† that by the action of ICl on oleic acid HCl forms not by its splitting off from an ICl-addition product but because of direct substitution by the action of the decomposition products of ICl. Addition of HCl (H ions) up to a certain concentration drives back the

* Of the large number of investigators who have worked with the Hübl iodine value, should be mentioned: Hübl, Ding. Polyt. Jour., **253**, 281; Liebermann, Ber., **24**, 4117 (1891); Schweissinger, Pharm. Zentraln., No. 12, 147 (1887); Benedikt, Chem. Ind., No. 8 (1887); Merkling, Chem. Ztg., **11**, No. 22 (1887); Bruche, Apoth. Ztg., **1890**, 493; Holde, Mitteil., **9**, 81 (1891) and **10**, 163 (1892); Fahrion, Chem. Ztg., **15**, 1792 (1891) and **16**, 863 (1892); Gautter, Ztsch. anal. Chem., **1893**, 303; Ephraim, Ztsch. für angew. Chem., **8**, 254 (1895); Schweitzer and Lungwitz, Jour. Soc. Chem. Ind., Feb. and Dec., **1895**; Waller, Chem. Ztg., **19**, 1786, 1831 (1895); Wijs, Ztsch. f. angew. Chem., **11**, 291 (1898); Chem. Rev., **6**, 1 (1899); Hanus, Ztsch. f. Nahr. u. Genussm., **1901**, 913; Ingle, Jour. Soc. Chem. Ind., **1902**, 587 and **1904**, 422.

† Chem. Zentralbl., **1912**, II, 1154.

substitution; large amounts however may cause adding onto the double bond. Excess of iodine drives back substitution by chlorine. The Wijs iodine solution is therefore suited for the determination of the iodine value, as acetic acid (Waller's solution contains HCl) does not act on the double bond, and yet has a sufficient H-ion concentration to prevent substitution.

The structure of the acids* is of great importance in determining the amount of absorption. The farther the double bond is removed from the carboxyl group, the more nearly do the iodine values found approach the theoretical values; thus for oleic acid

$$CH_3 \cdot (CH_2)_7 \cdot CH: CH \cdot (CH_2)_7 \cdot COOH,$$

the found and calculated values are the same; crotonic acid

$$CH_3 \cdot CH : CH \cdot COOH$$

has an iodine value of 4.3 to 17.4 while the theoretical is 295; the acid

$$CH_3 \cdot (CH_2)_{14} \cdot CH : CH \cdot COOH$$

has the actual value 3.0 to 18.0, the theoretical being 89.7.

Variations of the Iodine Value. The method of preparing oils by nature rich in solid glycerides has a great influence on the iodine value (bone oil, neat's-foot oil, peanut oil). According to the use of the oils, the solid glycerides are more or less pressed off in the treatment; the more complete this removal, the higher will be the iodine value. The bone and neat's-foot oils for fine mechanisms must be clear and liquid at fairly low temperatures and are therefore freed to a large extent from solid glycerides; these oils consist of almost pure olein and have the highest iodine values of all commercial neat's-foot oils (oils solid at room temperature have iodine value of about 44, oils liquid at $-10°$ have iodine values up to 75). Other methods of treatment, as shown by Negri and Fabris, influence the absorptive ability of oils; thus olive oils, extracted with solvents, contain more solid glycerides and consequently have lower iodine values. Many oils are artificially thickened by blowing in air; such oils, by absorbing much oxygen, with the formation of oxy-acids, show lower iodine values (down to 55). Linseed oils after boiling with insufficient air polymerize and in so doing decrease their ability to absorb iodine.

The iodine value of an oil will change on standing. Therefore in determining the iodine value, especially of drying oils, one must con-

* Poncio and Gastaldi, Gaz. Chim. Ital., **42**, II, 92 (1912); Zentralbl., **1912**, II, 1154.

sider also the specific gravity of the oil as well as its content of oxy-acids, which rises in old oils, to avoid making wrong conclusions from a consideration of the iodine values alone. Thus the iodine value of the non-drying olive oil, which originally was 85, sank to 81 after 19 months in a closed flask; a rape oil kept 7 months in an open dish changed from iodine value 98.3 to 88.4; a mixture of rape and cottonseed oils dropped from 95 to 76; a poppy-seed oil from 141 to 94.2. The specific gravity of the olive oil changed from 0.914 to 0.916 at 15°, of the rape oil from 0.914 to 0.925, the mixture of rape and cottonseed oils from 0.915 to 0.933, that of the poppy-seed oil from 0.924 to 0.963. These changes in the iodine values and specific gravity can be attributed* to changes of the double bonds by oxidation, polymerization and anhydride formation. As a consequence these oils also become decidedly more viscous.

To determine the iodine value of a semi- or non-drying oil, which has been changed by the atmospheric oxygen, a correction† of 0.8 should be added to the value found for every 0.001 increase at 15.5° in the specific gravity; if the original specific gravity is not known, an average value for the oil is taken. The results obtained by this method are satisfactory in many cases, but in some instances, the deviations are considerable.

Determination of the Iodine Value by the Hübl-Waller Method.

(α) **Iodine Solution.** 25 grams of iodine and 30 grams of mercuric chloride are each dissolved in 500 c.c. of 95 per cent alcohol; the filtered solutions are united and mixed with 50 c.c. of hydrochloric acid of specific gravity 1.19. The solution thus obtained is more stable than the one originally used by Hübl, since the HCl unites with the water, and secondary changes in the Hübl solution, by which hypo-iodous acid is formed, are avoided.

$$ICl + H_2O \rightarrow HCl + HOI.$$

(β) Sodium thiosulphate solution is prepared by dissolving 24.8 grams of salt in 1 liter of boiled water, its titer being determined as follows; the result should be checked from time to time.

20 c.c. of a stock solution of potassium bichromate (3.8663 grams in 1 liter) are run into a glass-stoppered bottle containing 10 c.c. of potassium iodide solution and 5 c.c. of conc. hydrochloric acid; this will cause the liberation of 0.2 gram of iodine, which is then titrated with sodium thiosulphate. The latter being run in till the solution is only faintly yellow, a few drops of starch solution are added and then finally sodium thiosulphate drop by drop with constant shaking until the last drop just causes the disappearance of the blue color.

* Mulder, Die Chemie der trockenden Oele usw., Berlin, 1867; Hazura, Monatshefte f. Chemie, **1888**, 180, 198; Fahrion, Chem. Ztg., **17**, 684, 1848 (1893).

† Sherman and Falk, J. Amer. Chem. Soc., **25**, 711 (1903); **27**, 605 (1905); Chem. Ztg., **27**, 217 (1903).

(γ) The potassium iodide solution contains 1 part potassium iodide to nine parts of water.

Procedure. Samples which contain impurities or are not clear must be freed from these by filtration; bone oils and other oils, which contain solid fat particles, like palmatin and stearin in suspension, also tallow, lard, etc., are purified by filtration in a hot water funnel. Solid fats are weighed in a small vessel containing a glass rod, the fat is then melted, a few drops are run out, the vessel cooled and then reweighed.

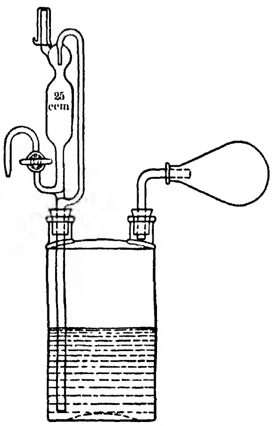


FIG. 129

The oil (0.18 to 0.22 gram, 6 to 8 drops of liquid fat, 0.5 to 1.0 gram of solid fat or 0.15 to 0.18 gram of a drying oil) is placed in a 300 c.c. glass-stoppered bottle with 20 c.c. chloroform and to the solution are added 25 c c. (30 c.c. with a drying oil) of the mercuric chloride-iodine solution; there should be at least 50 per cent excess iodine, since otherwise the iodine values will be too low. An arrangement shown in Fig. 129 may be used to measure off the 25 c.c. quantities. The mixture is well shaken and then allowed to stand for 24 hours protected from direct sunlight. If the solution becomes cloudy more chloroform is added. At the same time two blank tests (20 c.c. chloroform and 25 or 30 c.c. of iodine solution without oil) are started and allowed to stand the same length of time. After 24 hours the amount of free iodine is determined by adding 20 c.c. of the potassium iodide solution and 100 to 150 c.c. of water and then titrating with sodium thiosulphate. The difference in the amount of iodine contained in the one bottle containing oil and the one containing none gives the amount of absorption. The return of the blue color after standing, due to the splitting off of iodine from the addition product, should not be considered.

Example. 0.1945 gram of linseed oil is treated with 30 c.c. of iodine solution. 1 c.c. of sodium thiosulphate is equivalent to 0.011572 gram of iodine. After 24 hours, 30 c.c. of oil-free solution required 62.19 c.c. of sodium thiosulphate; 30 c.c. of the solution containing oil required 33.39 c.c. of thiosulphate. The iodine absorption was therefore equivalent to 62.19 c.c. less 33.39 c.c. or 28.80 c.c. of thiosulphate; or 0.1945 gram of linseed oil have absorbed (28.8) (0.011572) or 0.3333 gram of iodine. The iodine value is $\frac{(0.3333)\ (100)}{0.1945} = 171.3.$

In case time is lacking, the iodine is allowed to act only two hours; in this case, 30 c.c. of iodine solution will be required for non-drying oils, 40 c.c. for semi-drying and 60 c.c. for drying oils, in order that the same values may be obtained as would be obtained after 24 hours treatment.

Use of the Older Hübl Iodine Solution is prescribed in the German customs house examination of fatty oils. It differs from the

Waller modification of the Hübl in that the 5 per cent iodine and 6 per cent mercuric chloride solutions are kept separate and are mixed previous to use, but no hydrochloric acid is added. The mixing should take place at least 48 hours before use; otherwise the method is carried out as described above (0.3 to 0.4 gram oil in 15 c.c. chloroform and 30 c.c. of iodine solution). The Hübl iodine solution is to be used only so long as 25 c.c. require at least 35 c.c. of N/10 thiosulphate (the amount of free iodine contained comes less on standing).

Determination of the Iodine Values According to Wijs. The disadvantage of the Hübl-Waller method is the long time required for an experiment; this is overcome by the method of Wijs* in which a $\frac{N}{5}$ solution of iodine monochloride is used.

7.8 grams of iodine trichloride and 8.5 grams of iodine are dissolved in warm glacial acetic acid and the combined solutions are made up to 1 liter. Carbon tetrachloride (commercial chloroform frequently contains alcohol) is used to dissolve the fats. The carbon tetrachloride is to be treated with potassium bichromate and conc. sulphuric acid to test for oxidizable substances; a green color should not appear. The method of procedure is the same as described under the Hübl. With non-drying oils with iodine value under 100, one-half hour is sufficient to finish the reaction; with semi-drying oils, one-half to one hour is required; while with drying oils, one to two hours are necessary.

The Wijs method, which gives in the case of pure fatty acids values agreeing well with the theoretical, has found favor industrially. With non-drying and semi-drying oils, the Wijs values are several units higher than those obtained by the Hübl-Waller method, while with drying oils the Wijs values may be 10 units greater; in the case of wool fat and the unsaponifiable part of wool-fat olein, the difference is at times as great as 34 units.

Method of Winkler.† This is simple, direct, and inexpensive. With fats of iodine value less than 100 a 0.2 to 0.5 gram sample is used (an iodine value 100 to 150 needs 0.15 to 0.20 gram, while an iodine value over 150 requires only 0.10 to 0.13 gram of oil).

The sample is dissolved in 10 c.c. of carbon tetrachloride, 25 c.c. of a $\frac{N}{5}$ bromate-bromide solution (containing 5.568 grams of potassium bromate and 40 grams of potassium bromide in one liter of solution) are added, and then 10 c.c. of 10 per cent of hydrochloric acid. The flask is tightly stoppered and well shaken, then allowed

* Ber., **31,** 750 (1898); Ztschr. f. anal. chem., **1898,** 277; Chem. Umschau., **5,** 120, 137 (1898) and **6,** 5 (1899); Chem. Ztg., **38,** 1111 (1914).

† Z. Nahr. -u. Genussm., **28,** 65 (1914); **31,** 382 (1916). Chem. Ztg., **39,** 744 (1915).

to stand 2 hours in the dark (with low iodine values, only 30 min.; with train oil, 4 hours). The stopper is then removed, 10 to 14 c.c. of a 10 per cent solution of potassium iodide and 150 c.c. of water are added, the flask shaken, and the iodine titrated with $\frac{N}{10}$ sodium thiosulphate solution.

This method gives the same values with oils as the methods of Hübl or of Waller. It is said that while crotonic, tiglic, and cinnamic acids give by the methods of Waller and Wijs and of Hübl quite misleading values, this method of Winkler gives values corresponding to the calculated.

8. **The Acetyl Value.** This represents the number of milligrams of potassium hydroxide required to neutralize the acetic acid split off in the saponification of 1 gram of acetylated fatty acid or acetylated fat or wax. It is used to determine quantitatively the hydroxyl content of a substance and can be used as a measure of the amount of oxy-acids or fatty alcohols and mono- and di-glycerides in a fatty product. Every alcoholic hydroxyl group takes on an acetyl group on boiling with acetic anhydride and on subsequent saponification splits this off again. In the examination of lubricating oils, the acetyl value is determined when the degree of oxidation of boiled or blown oils or the amount of castor oil or grape-seed oil (both of which consist essentially of glycerides of oxy-acids) is to be estimated (see page 413, petroleum ether-insoluble oxy-acids). Also in scientific investigations, for example, to determine the amount of mono- and di-glycerides in the partial saponification of fats, the acetyl value is of importance. Castor oil has the acetyl value 153 to 156, grape-seed oil 144, the other fats less than 10; only in old or rancid fats will it be higher.

(α) **Acetylation According to Benedikt-Ulzer.*** 15 grams of non-volatile, water-insoluble acids, obtained from the fat by the method of page 406 are boiled with an equal volume of acetic anhydride for two hours under a reflux condenser; the mass is rinsed into an Erlenmeyer flask with 500 c.c. of water, 3 times boiled with fresh portions of water over a free flame to remove the acetic acid, the water removed after each boiling by means of a separatory funnel. To avoid bumping, a stream of carbon dioxide is led to the bottom of the beaker through a capillary. The free acetic acid is generally removed by three washings with water (test with litmus). The acetylated acids are dissolved in ether, then filtered and the solvent evaporated.

(β) Holland† prepares the acetylated acids by heating 5 grams of fatty acids with 10 c.c. of acetic anhydride for 1.5 hours in a boiling water bath; then enough ceresine (of saponification value equal to 0) is added to make a solid cake on cooling, from which the water may easily be poured. The cake is then shaken with 150

* Monatshefte, **8**, 40 (1887).

† J. Ind. Eng. Chem., **6**, 482 (1914). Seifensiederztg., **42**, 49 (1915).

c.c. portions of water (which are decanted after cooling) until all excess acetic acid has been removed.

(γ) **Saponification of the Acetylated Acids According to Lewkowitsch.** 4 to 5 grams of the acetylated acids are saponified by boiling with 50 c.c. of N/2 (preferably methyl) alcoholic potash under a reflux condenser; the alcohol is then evaporated, the soap dissolved in boiled water and enough N/2 sulphuric acid (determined by a blank test) to neutralize the alkali is added. To hasten the separation, a measured excess of the acid is used. The separated acids are filtered (see Hehner value) and washed with hot water till this no longer gives an acid reaction with methyl orange. In the total filtrate, the freed acetic acid is titrated with N/10 alkali. The number of c.c. of alkali used (subtracting the equivalent of the excess of sulphuric acid added), multiplied by 56.11 and divided by the amount of substance used, gives the acetyl value.

9. **Gravimetric Determination of the Oxy-acids.** The amount of oxy-acids present in an oil may also be approximately determined by weighing* the acids insoluble in petroleum ether; however, not all oxy-acids are insoluble in petroleum ether. The method is used to compare the degree of oxidation of linseed oil varnishes and blown oils, as well as to determine the amount of oxidized acid in degras. It is carried out as follows:

5 grams of fat are saponified with 25 c.c. of N/1 alcoholic alkali; after evaporation of the alcohol, the soaps are dissolved in 70 c.c. of hot water and are then acidified with dilute hydrochloric acid in a separatory funnel. After cooling, the mass is extracted with 100 c.c. of petroleum ether; after standing over night, the ether solution becomes clear, the oxy-acids adhere to the walls of the funnel and can easily be separated from the aqueous and petroleum ether layers. They are well washed with petroleum ether, dissolved in warm alcohol, dried at 105° after evaporation of the alcohol and weighed. If the amount is considerable, they may still contain unoxydized acids; in this case it is advisable to redissolve in alkali and to re-separate the oxy-acids by treatment with petroleum ether and hydrochloric acid.

This method is not applicable to the determination of the fatty acids of castor oil, since the acids, by themselves insoluble in petroleum ether, lose their insolubility in the presence of other fatty acids.

Zerewitinoff† has suggested another method for the determination of oxy-acids. This depends on the use of magnesium-organic compounds. A pyridine solution of the fatty acids is treated with a solution of magnesium methyl iodide in amyl ether. In this way methane is evolved quantitatively, but the hydroxyl groups of the carboxylic acids also react; the latter must be determined in a separate experiment. This method has not been used industrially.

10. **Hexabromide Value.** This is the number of grams of hexabromide obtained from 100 grams of fatty acid. It is a measure of the

* Fahrion, Zeit. f. angew. Chem., **11**, 782 (1898).

† Z. analyt. Chem., **52**, 729 (1913).

amount of linolenic acid (oleic, linoleic and isolinolenic acids are not precipitated). Hazura first (page 375) carried out experiments on the bromine addition products of the unsaturated acids. Hehner and Mitchell* used the method in the quantitative examination of oils, by allowing bromine in ether-glacial acetic acid solution to act on the oil; since, however, evaporation of ether took place owing to the temperature rise, the amount of hexabromide separating was variable. Recently the various sources of error have been studied by Eibner and Muggenthaler† and the following is their procedure:

Preparation of the Pure Fatty Acids. In each of three 220 c.c. evaporating dishes, 3.5 grams of oil are saponified with 45 c.c. of N/2 alcoholic potash by heating on a water bath, stirring frequently; the resulting soaps are then completely freed from alcohol. The first dry soap is dissolved in 50 c.c. of hot water and then rinsed into the second dish, and from this into the third. The combined solutions of less than 180 c.c. are put into a 1 liter separatory funnel and after cooling, the fatty acids set free by adding 20 c.c. of 5 N sulphuric acid, are extracted with 100 c.c. ether. The lower layer is run into a second separatory funnel and extracted with 40 c.c. of ether. The combined ether solutions are then dried with anhydrous sodium sulphate for at least 5 hours, best over night. After drying, the solution is run through a dry filter paper. The ether is then distilled from a 200 c.c. Erlenmeyer flask closed with a two-hole stopper; one hole carries a separatory funnel to add fresh portions of wash-ether, the other is attached to a condenser. The ether distilled off is used to wash the Glauber's salt (which absorbs much of the ether solution) with five or six 100 c.c portions of ether, the paper being finally washed in the same way. When ether no longer distills, the funnel and condenser are disconnected and gas inlet and exit tubes are attached, the inlet tube reaching nearly to the bottom, the outlet tube being drawn out to a capillary. A stream of hydrogen (purified by passing through alkaline lead acetate and through conc. sulphuric acid) is run at a rate of 5 bubbles per second over the residue heated on a water bath. The flask is then put warm into a vacuum desiccator, which is evacuated. After 4 hours the flask is quickly weighed and again desiccated and weighed after 2 hours; it is again placed in a desiccator which is evacuated and left over night when the weight is again determined.

Preparation of the 10 per cent Solution of the Fatty Acids. From the weighed fatty acids (9 to 10 grams) a 10 per cent solution is prepared by adding 40 c.c. of ether (dried over calcium chloride and then filtered) to the flask, dissolving by gentle agitation and then making up with ether to exactly 100 c.c. in a graduated flask.

Method of Bromination. Twenty c.c. of the ether solution of the fatty acids (containing 1.9 to 2.0 grams) are placed in a 100 c.c. Erlenmeyer flask closed with a cork with a groove cut in the side, the flask being placed in a freezing mixture and kept 10 minutes at − 10°. One c.c. of bromine is then added drop by drop along the sides of the flask, the first 0.5 c.c. being added in not less than 20 minutes, the last 0.5 c.c. in not less than 10 minutes. It is then shaken and left for 2 hours in a freezing mixture which never gets warmer than − 5°. In the meanwhile 5 test tubes,

* Analyst, **23,** 313 (1898).

† Farbenztg., **18,** 131, 175, 235, 356, 411, 466, 523, 582, 641 (1912).

each containing 5 c.c. of ether, are placed in the cold bath. A Gooch crucible with asbestos mat is then prepared, dried at 110° and weighed. The separated hexabromide is first washed by decantation and is then transferred to the crucible in a quantitative manner; the cooled ether is used to wash the precipitate and to bring about its transfer. Suction should not be applied during the filtration until the last bit of liquid has run through; at the end the precipitate is sucked dry, the crucible wiped dry on the outside and then dried for two hours at 80 to 85°. It is allowed to cool in a desiccator and weighed. The hexabromide should be white, this color being attained by not allowing the precipitate to get dry during the filtration. The hexabromide is calculated on the basis of 100 grams of fatty acid. Results should check to within 1 per cent.

Pure white hexabromides obtained in this way had the theoretical bromine content and melted at 177°. The various linseed oils examined gave the hexabromide values stated in the following table:

TABLE 94

Source	Hexabromide values				Per cent linolenic acid in the fatty acids
	Commercial oils		Oils pressed in laboratory	Of oils with dark fatty acids	
	Limits	Average			
Holland	51 2 to 52.3	51 7		47 7	19 0
La Plata	50 4 to 52 7	51 7	52 2 to 54 3	48 5 to 50 6	19.0
India	50 1 to 50 9	50 5	50 7 to 54 6	50 7	18.5
Baltic	58 0	58 0	58 5 to 59 1	52 4	21 3

These figures were given by Eibner and Muggenthaler; they have not, however, shown cause for excluding from the average values the results obtained with oils pressed in the laboratory or with oils containing dark fatty acids; the true average is thus in question until this point is settled (Eibner is working on this matter).

Varnishes give lower hexabromide values than do linseed oils, the values ranging from 46.7 down to 39.7; the longer an oil has been boiled the lower will be this value. Polymerized oils (see page 410) give hexabromide values under 2 although the iodine values range from 100 to 126, from which it follows that, on boiling, mainly the linolenic acid is changed.

Of the other fatty oils which are used to adulterate linseed oil, poppy-seed oil and wood oil have the hexabromide value of 0; rape oil, 4.6 to 7.6, average 6.3; soja bean, 7.2; perilla oil, 64.1, which is equivalent to 23.5 per cent of linolenic acid.

11. **Oxygen Absorption.** In determining the liability of an oil to spontaneous combustion, the ability of the oil to absorb oxygen is of importance (see page 189); this test is also of value in distinguishing drying, semi-drying and non-drying oils. Since oleic acid is not a drying component, while linoleic and linolenic acid and their glycerides are active dryers, a high iodine value indicates a drying oil

To determine the drying power one drop of oil is spread over a glass plate, 5 cm. by 10 cm., and kept at 50° in a drying closet, or simply left at room temperature. The consistency is determined from time to time and the appearance of a dry, thick skin watched for.

The semi-drying oils require 7 to 10 days for drying; rape oil which is between a semi-drying and a non-drying oil, gets very viscous and sticky after 12 days. Of the drying oils, poppy-seed oil requires 6 days, linseed oil, 3 to 4 days, varnish and wood oil will be dry after one day. The temperature, humidity and light intensity effect the outcome of the test (page 486).

Attempts have been made to measure the oxygen absorption quantitatively, although none of the methods have attained much importance. This is, in part, due to the fact that when oxygen is absorbed, water and carbon dioxide will be split off and fatty acids of low molecular weight and aldehyde-like bodies will form.

In the method of Livache* the oil is allowed to oxidize in a thin film under the catalytic influence of lead. The finely-divided lead is prepared by precipitation from lead acetate solution with zinc, washing with water, alcohol and with ether and drying in a vacuum. One gram of powder is put on a watch glass and 0.7 gram oil is dropped on the lead so that the drops do not run together. These samples are allowed to stand at room temperature and exposed to light; the maximum weight is determined, this being attained generally in 18 hours with drying oils, the non-drying oils requiring 4 to 5 days to show an increase in weight. After two days the increase in weight with linseed oil was 14.3 per cent; walnut oil, 7.9; poppy-seed oil, 6.8; cottonseed oil, 5.9; on the other hand 0.0 per cent for olive oil, rape oil, peanut oil and sesame oil.

In the method of Weger and Lippert,† the oil is spread in a thin film over glass plates (0.0004 to 0.0008 gram on 1 sq. cm.) and weighed from time to time. The results are higher than those of Livache; it appears to be a more practical test but is not very accurate, since the weighings should be made to hundredths of a milligram.

XV. Short Review of the Procedure in Testing Fatty Oils Free from Mineral Oil

With all fatty bodies, after making a qualitative test of saponifiability or after separating unsaponifiable matter by the method of Spitz and Hönig, the iodine and saponification values are determined;

* Compt. Rend., **102**, 1167 (1886). † Ubbelohde, Bd. I, 274.

these values allow a classification of the oil by means of the points developed in the preceding pages and Tables 95 to 101. Iodine values above the normal ones for olive, rape and neat s-foot oils at once suggest an adulteration. Iodine values over 85, with saponification values under 188, point to rape oil. A low saponification value is, however, characteristic of all crucifer oils, as well as for castor oil and the so-called liquid waxes. The oils mentioned, and rape oil, can be distinguished by the petroleum ether extract of the soap solution (liquid waxes contain considerable amounts of vaseline-like higher alcohols), odor (liquid waxes have a peculiar fish-like odor), solubility in 90 per cent alcohol, as well as in petroleum ether, high viscosity (the last three tests characterize castor oil), the erucic acid test, etc. If in an olive oil a normal saponification value and an iodine value over 80 is found, the Baudouin and Halphen tests for sesame and cottonseed oils are made. If these oils are absent, the solubility of the potassium soaps in alcohol is determined according to Tables 95 to 101; if no precipitate is shown at 18° C. after standing ½ hour, more than 15 per cent of peanut oil is not present. Cloudiness without precipitation may arise with pure olive oil; if a precipitate forms, the amount of arachidic acid is determined and if more than 0.2 per cent is found, peanut oil may be present.

As with olive oil, so also with other fatty oils (neat's-foot and rape oils), after determining the acidity, the iodine and saponification values should be established and then the further tests applied. To detect vegetable oil in animal oil, the phytosterin acetate test is made (page 399).

With oils having a high acidity, the iodine and saponification values of the fatty acids only are to be determined; the Baudouin and Halphen tests may also be applied to these. A saponification value below the normal for olive oil, neat's-foot oil and bone oil, if the specific gravity is also low (under 0.910), points to the presence of liquid waxes, which may, however, be characterized by means of their unsaponifiable alcohols of high molecular weight. A low iodine value in olive, rape and bone oils, if the specific gravity is beyond the normal limits, points to thickening of the oil; in this case the viscosity and content of oxy-acids give valuable information. The increase in oxy-acids need not run parallel with the iodine value, since the thickening may have been due to polymerization as well as oxidation.

Specifications for Torpedo Lubricating Oil*

The oil must be a mixture of pure bone and refined rape oils; it should be light yellow and clear in color, and should have only a faint

* Kaiserl. Torpedowerkstatt Friedrichsort.

odor. Its specific gravity at 15° should fall in the limits 0.913 and 0.917; its viscosity (Engler degrees) at 20° should be between 12.0 and 13.5.

A portion of the oil cooled to − 10° for four hours should remain clear and liquid; another portion cooled four hours to − 15° should be still salve-like; an oil remaining liquid is preferred. The Pensky-Martens flash point should be over 200°; the iodine value, 77 to 84; the saponification value, 185 to 190. The acidity should not be more than 0.14 per cent calculated as oleic acid; on the average it should be free from acidity. Rosin oil, tar oil and mineral oil should be absent.

Specifications for Fatty Oils (Royal Powder Mills, Spandau)

I. Linseed Oil

The oil (prepared cold) should be yellow to brown, clear and free from non-drying oils, rosin or other impurities; organic acid, under 2.12 per cent (calculated as oleic acid); specific gravity at 15° not under 0.930; iodine value, not under 171.

If a 5 c.c. portion of linseed oil is boiled for 3 minutes, shaking continuously, with 0.25 gram potassium permanganate, a drop, after cooling, spread with the finger in a thin layer over a glass plate, after six hours heating to 100° should dry to a brilliant surface, which should no longer be sticky after cooling.

II. Olive Oil

The oil should be pure and not mixed with other substances; should be clear and without rancid odor and on standing should not deposit a sediment. Mineral acid should be absent; organic acid should not be present in quantity greater than 2.12 per cent oleic acid. Specific gravity at 15°, 0.914 to 0.920.

III. Neat's-Foot Oil (Bone Oil)

(*a*) **Oil for Use in Works.** The oil should be mobile, pure and free from foreign oils and mineral acid and should not deposit a sediment on standing. Cooled to 0°, no solidification should take place after standing one hour. Organic acid should not be present in quantity greater than 2.12 per cent oleic acid. Specific gravity at 15°, 0.914 to 0.917. A drop on a glass plate in a thin layer and kept for 24 hours at 50° in contact with air, should, on cooling, show no resinous material or tendency to dry, but should move easily under the finger.

(*b*) **Oil for Firearms.** The purified and filtered oil should appear clear in a test tube 15 mm. wide (light yellow). It should not be mixed with any oil, nor should it deposit a sediment on standing, nor should it have a bad odor. It must remain liquid after 1 hour at − 10°. Organic acid, less than 2.12 per cent oleic acid; specific gravity, 0.914 to 0.917 at 15°; viscosity (Engler), not under 12 at 20°; saponification value, 190 to 200; iodine value, 70 to 82. A drop of oil exposed as above should conform to the same conditions.

TABLE 102

SPECIFICATIONS FOR RAPE OIL AND LINSEED OIL

	State	Specific gravity, 15° C. ×1000	Behavior in cold	Acid content, per cent oleic acid	Further properties
Rape oil (for machinery)	Prussia, 1907	. .. ..	..	Under 2.1	Free from mineral acid, mucilagenous material and foreign admixtures, non-drying, no sediment on standing.
	Bavaria, 1907	910 to 915	.	Under 2.1	Pure rape oil, clarified, free from water and mucilagenous material.
	Saxony, 1903	... .		.	Pressed from pure material, free from admixture, all resinous materials removed, allowed to settle 3 months, must be non-drying and not sticky, must not deposit residue on standing.
	Wurttemberg, 1910	....	. .	.	Should not attack the lubricated parts, must not thicken or resinify, otherwise like lamp oil. (Is only rarely used for lubrication.)
	Baden, 1910	To 913	No separation at 0° C. even after some time	Under 2.24	Refined rape oil meeting all the specifications of a lamp oil. Engler viscosity at 20° at least 12.
	Imperial Territory, 1903	. .	.		See specifications for lamp oil.
	Royal Powder Works, Spandau, 1911	913.2 to 917.5		Under 2.1	On shaking the oil with the same volume of sulphuric acid (sp. gr. 1.53) no green color should form. Otherwise like Prussian specifications.
Rape oil (for lamps)	Prussia, 1907	913 to 917	No solid separation at 0° C.	Under 2.1	Best oil, free from water, resin and mucin. Traces only of mineral acid, no foreign admixtures, no deposit on standing, burning with a bright, white flame, without odor or soot.
	Bavaria, 1908	....	... ..	Under 1.82	Should be pure material, not flashing under 120° (Pensky), burning (in lamps with 17-mm. wide wicks and 25-mm. high flame) with a white, bright flame without soot and no crust should form after 6 hours burning, consumption per hour 7 grams at most, 1.5 candle power after 10 hours, no distillation products under 200°.

TABLE 102 (*Continued*)

Rape oil (for lamps)	Saxony, 1903	....	. . . .	. . .	Burning with a bright flame without odor, or soot, otherwise like machinery oil.
	Baden, 1910	To 913	No separation at 0° C. even after some time	Under 2.24	Refined, clarified rape oil free from water, mucin, impurities and other oils, no sediment on standing, burning with a bright, white flame without odor and soot. With $\frac{1}{8}$ of its volume of sulphuric acid (sp. gr. 1.53) the oil must give an uncolored emulsion; on shaking with alcohol, the latter must remain colorless. Mixed with $\frac{1}{8}$ its volume of sodium hydroxide (sp. gr. 1.43), it must give a white or faint yellow emulsion. It must be completely saponifiable with KOH or NaOH, the soap formed must be white or faint yellow. A drop of oil on a brass plate must show no resinification on evaporation and should show no green color within 24 hours.
	Imperial Territory, 1903	....	Remelting clear after freezing	Under 2 per cent calculated as oleic acid	Purified and settled rape oil, free from mineral acid, resin and mineral oil, no sediment on standing, burning on lamps without a chimney for 5 hours with a bright, white flame without carbonization, capable of being used for lubrication, without attacking the lubricated surfaces, without thickening or resinification.
	Württemberg	....	. . . ...		Does not use rape oil for illumination.
Linseed oil	Prussia, 1901	930 to 940 20°	. ...		Settled, free from mucin and foreign admixtures, giving no sediment on long standing, forming a dry adherent film on glass or porcelain within 5 days at 20° C.
	Württemberg, 1904	. ...	.. ....	.	Pure, free from mucin and sediment on settling, drying easily.
	Baden, 1910	Between 28 and 29 (Fischer balance)	Liquid at −15°	. . .	Purified, yellow to brown yellow color, clarified, settled, must not become cloudy nor form a sediment on settling, free from rosin, rosin oil, non-drying and animal oils. A varnish of 1 part of lampblack and 3 parts of boiled linseed oil painted on glass plates placed vertically must after 2 days at 17 to 22° become a hard film at the top.
	Imperial Territory, 1912	930 to 955	....	....	Clear, settled, free from mucin, cold-pressed, light yellow color, no rancid odor or taste.

TABLE

VEGETABLE NON-DRYING

(The less common values enclosed in brackets.)

Kind of oil.	Viscosity (Engler) at 20°C.	Index of refraction 20°	Specific gravity at 15°	Solidification point 0° C.	Saponification number	Iodine value		Reichert-Meissl value***
						of the oil	of the fatty acids	
Olive oil, from the flesh of olives, *Olivenöl or Baumöl Huile d'olive.*	11 to 13	1 467 to 1 471 61 7 to 68 scale divisions	0 9140 to 0 9190, less valuable 0 9200 to 0 9290	Some still liquid at −5, solid at −9; others solid at 0°	189 to 196 (185) generally near 190	79 to 85 (88 7) 76 6 Japanese oil	86 to 90	0 2 to 0.8
Olive kernel oil, † *Olivenkernöl, Huile de noyeau d'olive*	...	25° 1 4682 to 1 4688	0 918 to 0 920	.	182 to 188 5	87 to 88		....
Peanut (arachis)‡ oil, *Erdnussöl, Huile d'arachide*	10 to 12	1 468 to 1 472 63 2 to 69 5 scale divisions	0 9163 to 0 9200	Generally solid at 0°	189 to 194	86 to 98 (103)	96 to 103	0 4 to 1 6
Lycopodium fat *Bärlappöl* ††	.	1 467	0 936		195	81	91 8	7 3
Japanese tea oil *Teesaatöl* φφ		1 468 to 1 471	0 916 to 0 917	−12 to −15	190 to 194	80 to 91		0 66
Castor oil, *Rizinusöl, Huile de ricin*	139 to 140	1 477 to 1 478 77 5 to 79 4 scale divisions	0 9613 to 0 9736	−10° to −18°	176 to 183 (186.6)	82 to 88	86 to 93	0 2 to 0 3 1 1 to 2 8
Grape seed oil, *Traubenkernöl, Huile de pepins de raisins*			0 9202 to 0 9561	−11° to −17°	178 to 179 189 5 to 194.4¶	94 to 96 143** 130 to 140¶	99	0 46
Curcas oil. xx *Kurkasöl, Huile de Pignon d'Inde*	. ..	25° 1 4681 to 1 4870	0 9192 to 0 9210	−8°	193 2 to 200 4	89 3 to 110	105	0 55

* Analyst, **1896**, 328. The author separated the stearic acid according to page 373. The result is not free from criticism.

† An oil with an iodine value of 95 is known on the market as Morocco oil, but it is not obtained from the olive but from a variety of nut grown in Morocco. The so-called Java olive oil is likewise not obtained from olives (Sasserath, Zeit. f. Nahr. und Genussmit, **20**, 749 (1910)).

‡ Brazil nut oil (Bertholethia excelsa) specific gravity 0.918, solidification point 0°, saponification value 193.4, iodine value of fatty acids 106.0, melting points of acids 28° to 30°.

§ According to Hehner and Mitchell 7 per cent stearic acid; according to Hazura (Monatshefte, **10**, 242) some hypogaeic acid ($C_{16}H_{30}O_2$). Monatshefte **34**, 1195 (1913).

|| Compt. Rend., **72**, 1330. Also Tortelli and Ruggeri. Chem. Ztg., **1898**, 600; Archbutt, J. Soc. Chem. Ind., **1898**, 1124.

*** Elsdon and Hawley, Pharm. J., **37**, 145 (1913). Chem. Ztg., **38**, 109 (1914).

95

Oils and Solid Fats

Vegetable non-drying oils and solid fats.

Acetyl value	Hehner value	Melting point of fatty acids °C.	Solidification point of fatty acids °C.	Behavior of the soap solution prepared according to page 388	Main components of the oil	Reactions and peculiarities
4 7	94 to 96	22 to 28 5 19 to 23 Californian oils	17 to 24 6	Generally clear at 18° to 20° Oils with little arachidic acid show a flocculent precipitate after ¼ to ½ hour standing	Olein, little linolein and considerable mixed glycerides containing much palmitic acid. According to Hehner and Mitchell stearic acid is absent.*	Arachidic acid present in small amount, up to 1 4% unsaponifiable components. Elaidin test yellow-white and hard.
22 5				.	Olein, little palmitin and stearin and no arachidic acid	It is more soluble in alcohol and glacial acetic acid than is olive oil probably because of its high content of fatty acids.
3 4	94 to 96	27 7 to 33	22 to 29 5	Gelatinized at 18 to 20°.	Olein, palmitin, stearin,§ arachin corresponding to 5% of arachidic acid, M P. 75°.	Detection of the oil according to Renard ‖ by isolating the "crude arachidic acid" (a mixture of arachidic acid and lignoceric acid.
44	87 6	39 to 40			81% lycopodic acid 3% dioxystearic 1% palmitic, 1% stearic, 2% myristic acid	.. . ...
.. .	95	38 5 22			7% solid, 93% liquid (oleic) acids.	Contains saponin, good for soaps, not as food.
150 to 154		13	3	Clear at 0°; 10% rape oil, peanut oil and cottonseed oil give flocculent precipitates.	Glycerides of ricinoleic acid (oxyacid) and its isomers, little stearin, oleic, unsaturated acids.‖ ‖	Miscible in all proportions with 95% alcohol, insoluble in petroleum ether and naphtha, 0 3 to 0 37% unsaponifiable.
144 5 (?) 44¶ fatty acids	92 to 97	23 to 25	18 to 20		13% solid acids, 80% liquid, palmitic, oleic, linoleic, erucic acids.	Color of oil, golden yellow to green.
17 6 to 34 7	95 5	24 to 26	28 6		10% solid acids M P., 57.5°, 10% linoleic, 10% oleic, 0.6 unsaponifiable.	Unpleasant odor. Dries in 24 hrs. belongs to semi-drying oils.

†† Rathje, Archiv. f. Pharm., **246,** 699 (1908).
‖ ‖ Fahrion, Chem Umschau, **23,** 60, 71 (1916).
φφ Taujimoto, J Coll Eng Imp Univ Tokyo, **4,** 75 (1908)
xx Klein, Z. angewandte Chem., **11,** 1012 (1898).
¶ Marre, Rev. chim. pure et appl., **1911,** 186; Zeit. f. angew. Chem., **1911,** 2033.
** Ulzer and Zumpfe find that grape-seed oil is easily soluble in petroleum ether, and that the lead salts insoluble in ether give 7 to 8 per cent of fatty acids of melting point 56° and iodine value 0 4, being a mixture of stearic and palmitic acids; the acids from the lead salts soluble in ether are shown (by oxidation with $KMnO_4$) to consist mainly of linolic and some oleic and ricinoleic acids. Lead salts insoluble in cold ether but soluble in hot ether are present only in traces; the separated acids give on oxidation an acid of melting point 115° (dioxybehenic acid and erucic acid M. P. 127°). Since the acid has an iodine value of 0.4, the assumption of Fitz seems incorrect.

TABLE

VEGETABLE NON-DRYING OILS

(The less common values are placed in brackets)

Kind of oil	Index of refraction	Specific gravity	Solidification point, °C.	Saponification value	Iodine value of oil	Iodine value of fatty acids	Reichert-Meissl value
Almond oil,* *Mandelöl*, *Huile d'amandes*	1 4728 15 5°	0 9160 to 0 9200	−10 to −21 5	190 to 196 (183), generally near 191	93 to 102	93 to 96	0 2 to 0 5
Cocoanut oil, *Kokosnussöl*, *Beurre de coco*	60° 1 441 40° 33.5 to 36.3 scale divisions	0 9250 to 0 9383	Becomes solid 14 to 23 1, melts 20.3 to 28	246 to 258 (268)	8.6 to 9 4, oil from rind 40	8 3 to 10, liquid acids 54	5 6 to 7 4 (8 4)
Palm** oil, from fleshy part of fruit, *Palmöl*, *Huile de palme*	60° 1 451 40° 47 scale divisions	0 9120 to 0 948	Melts according to age and source from 27 to 42 5	196 to 210	43 8 to 58	53.3, liquid fatty acids 95 to 99	0 5 to 1 9
Palm nut oil, *Palmkernöl*, *Huile de palmiste*	60° 1 4431 40° 36 to 36 5 scale divisions	0 9410 to 0 9520	Melts between 23 and 28	241 to 250	10 to 18	12 to 13 6	5 to 7
Vegetable tallow, from seeds of *Stilingia sebifera*, *Chin. Talg*, *Suif végétale de Chine*	Scale divisions at 50° 38	0 915 to 0 922	Trade samples 24 to 29, extracted with solvents 34	199 to 210	28 to 38	30 to 39	0 7
Cocoa butter, *Kakaobutter*, *Beurre de Cacao*	60° 1 4220	0 950 to 0 995	23 to 26, melts between 30 to 33	192 to 194 (200)	34 to 37, Bahia fat 38 to 41.7	32 6 to 39 1	0 3 to 1 6
Dika oil, from seeds of *Irvingia gabonens*, *Dikafett* *Beurre de dika*	...	(Schädler) 0 820	34 8, melts 29 to 31	244 5	30 9 to 31 3	.	0 42
Mowrah fat ϕ	40° 50.7 to 54.2	.. ..	16.6 to 22.4 M. P. 24.5 to 28.4	190 to 194	60 4 to 63 8	52 5	1 43 to 1 63
Shea fat ϕ	40° 57.5 to 61	. ....	21 to 25.2 M. P. 43.4 to 45.2	176 to 188	54 4 to 59 9	..	1 25 to 1 4
Sierra Leone butter ϕ	25° 1 4617 40° 45 to 46	0 9165 at 30°	24 to 38.5	190 to 197	42 to 46	43 to 47	0 22
Chaulmoogra oil***	....	0 903	17 8 M. P. 24.5	206	92	96	3.6
Mace butter, *Muskatbutter*, *Beurre de Muscade*	40° 1 4704	0 945 to 0 996	39 to 42, melts 38 5 to 51	153 5 to 161 (191.4)	40 1 to 59	....	1 0 to 4.2
Laurel oil, *Lorbeerfett*, *Huile de Lauriel*	....	0.9322	24 to 25, melts 32 to 36	197 to 198	68 to 80	81 6 to 82 0	1 6
Japan wax ϕϕ *Japanwachs*, *Cire du Japon*	....	0 970 to 0 980	48 5 to 53	217 to 237.5 (206.6 to 212)	4 9 to 12 8	42.1	1 2

* Apricot and cherry-kernel oils show constants very similar to those of almond oil.
† Bieber's reagent (fuming nitric acid, conc. sulphuric acid and an equal volume of water) 1 part and 5 parts of oil gives with almond oil a yellow-white, with apricot and cherry-kernel oil at once a cherry red color. See Chwolles, Pharm. Ztg., **1903**, 109.
ϕ Elsdon, Analyst, **38**, 442. Chem. Umschau, **20**, 60 (1913).
** Hebert, Z. angewandte Chem., **25**, 1653 (1912).
†† Power and Salway, J. Chem. Soc., **1907**, 2037; **1908**, 1653.

Acetyl value	Hehner value	Melting point of fatty acids, °C.	Solidification point of fatty acids, °C.	Main components of the oil	Reactions and other characteristics
5 8	96 to 97	12 to 14	9.5 to 10.1 (from sweet almonds), 11.3 to 11.8 (from bitter almonds)	Rich in olein, no stearin (Hehner and Mitchell, and Gusserow)	With nitric acid (sp. gr. 1.4) a faint yellow color, while apricot and cherry-kernel oils give an orange color.†
0 9 to 12 ϕ	82 4 to 90 5	24 to 27	15.7 to 20.4, titer test 21.2 to 25.2	Similar to palm nut oil, large amounts of myristin and laurin, smaller amounts of palmatin, olein, caprin, caprylin and caproin ϕ	Quite soluble in alcohol; 1 volume oil soluble in 2 parts of 90 per cent of alcohol.
1 8	94 2 to 97 0	44 to 50	35 8 to 45 6	Palmatin, olein, very little linolic acid 1 per cent stearic and acids of high molecular weight	Color between orange yellow and dirty dark red; large content of free acid (almost 100 per cent).
1 9 to 4 8	87 6 to 91 1	25 to 28 5	20 to 25 5	26 6 per cent olein, 33 per cent stearin, palmatin and myristin, 40 4 per cent laurin, caprin, caprylin and caproin	Color white, pleasant odor and taste (nutty).
.	93 5	Commercial samples 47 to 57; Extracted with solvents 39 to 40	42 to 52; 34 to 35	Palmatin and olein, 40.3 per cent stearin (Hehner and Mitchell)	Melting point of commercial samples of the fat, 44 to 46°; of samples extracted with solvents, 37 to 38°.
	94 6	48 to 52	45 to 47	Palmitin-stearic acid, oleic acid, arachidic acid, mixed glycerides	Bjorklund's ether test‡ S = 1.1 to 1.95 (10-year old sample S = 4.6).
				According to Oudemann laurin and myristin	With the Bjorklund test acts like cocoa butter.
.		44 5	42	.	$[\alpha]_D = +1.12°$.
	95 7	51 6 to 54 4	48 to 50 5		$[\alpha]_D = +3$ to $3.2°$.
....	96	57 to 57 5	51 5 to 54 5	Stearic acid; liquid acids $n_{40} = 38$. Iodine value = 87 3	White to golden yellow fat more solid than butter.
......	95	47 5	36 9	Chaulmagra acid, $C_{18}H_{32}O_2$, M. P. 68.5° (page 347); hydrocarpus acid, $C_{16}H_{28}O_2$, M.P. 60°	$[\alpha]_D = +41$ to $+64.5°$. Soluble in 3 to 4 volumes of 70 per cent alcohol. 3 grams of fat are poisonous.
......	. .	42 5	40 0	Trimyristin, 10 per cent essential oil ††	White color.
....	. . . .	. . ....	14 3 to 15 1	Trilaurin, olein	Green color, characteristic odor and taste.
27 to 31.2	90 6	56 to 62	53 to 56 5	Glycerides of palmitic acid, Japan acid ($C_{21}H_{40}O_4$), a volatile acid, free palmitic acid 11 to 14 per cent glycerine	....

‡ Zeit. f. analyt. chem., **3**, 233.

ϕ Z. Nahr. u. Genussm., **23**, 589 (1912); **27**, 723 (1914); **28**, 73, 247 (1914) Chem. Umschau, **17**, 263 (1910).

ϕϕ Fels, Seifenfabrikant **36**, 141 (1916).

*** Luhn Seifensiederstg., **37**, 1460 (1910); **38**, 51 (1911). Litterscheid, Chem. Ztg., **35**, 9 (1911). Plucker, Z. Nahr. u. Genussm., **21**, 257 (1911) Grimme, **18**, 133 (1911).

(The less common values are placed in brackets)

Kind of oil	Engler viscosity at 20°	Index of refraction, 20°	Specific gravity at 15°	Solidification point, °C.	Saponification number	Iodine value of the oil	Iodine value of the fatty acids	Reichert-Meissl value
Cottonseed oil, *Baumwollsaatöl* (*Cottonöl*), *Huile de Coton*	9 to 10 •	1 474 to 1 476, 72 7 to 76 scale divisions	0 9220 to 0 9300	Generally at 0°	191 to 198 generally near 195	102 to 111 (117)	111 to 116, liquid fatty acids 147 to 148	0 2 to 1
Kapok oil, *Kapoköl*,† *Huile de kapok*		at 25° 63 to 66 scale divisions	0 923 to 0 930	29 6?	189 to 197 (205)	118 to 119 74 to 108	98 7 to 112 3 (122 5)?	3 3
Sesame oil, *Sèsamöl*, *Huile de sèsame*	10 to 10 5	1 475 to 1 476, 74.3 to 76 scale divisions	0 9220 to 0 9237 (0 9210)	Between − 3 and −5	188 to 195	103 to 112 (117)	109 to 112	1 2 0 1 to 0.4
Corn (maize) oil, *Maisöl*, *Huile de mais*		15 5° 1 4768	0 9215 to 0 9239 (0.9262)	− 10 to −20	188 to 193	113 to 125	125, liquid fatty acids 141 to 144 ‡	0 33 to 2.5 §
Cameline oil, *Leindotteröl dtsch. Sesamöl* *Huile de cameline*		1 476	0 9228 to 0 9270 (0.9329)	−18	188	133 to 135	137	....
Soja bean oil, ‖ *Sojabohnenol*, *Huile de soja*	8 to 9	15° 1 4765 to 1 4775	0 9246 to 0 927	− 8 to −16	191 192 2 to 194	130 to 135 (121 to 124)?	131?	0.1 to 0.69
Pumpkin seed oil oil, *Kurbiskernöl*		25° scale divisions 70 to 72.5 (Poda)	0 9197 to 0 9250	−15	188 to 195	121 to 130		1 2 to 1 8
Beechnut oil, *Bucheckernöl*, *Huile de faine*		In Oleo refract. scale divisions 16.5 to 18	0 9205 to 0 9225	−17	191 to 196	104 to 120	114	. ....
Rape (Colza) oil, *Rüböl*, *Huile de Colza*	11 to 15 generally near 13	1.472 to 1 476, 69 5 to 76 scale divisions	0 9132 to 0 9175	Generally at 0° tallow-like, 5 to 10 hours cooling with stirring	171 to 179 (180) generally near 175	97 to 105 (108)	99 to 106, liquid fatty acids 121 to 126†	0 1 to 0.5
Black mustard oil, *Schwarzsenfsaatöl*, *Huile de moutarde noire*	. .	15 5° 1 4672	0 9160 to 0 9200	−5	174 to 175	96 to 107	110	. .....
White mustard oil, *Weissenfsaatöl*, *Huile de moutarde blanche*	..	15 5° 1 4750	0 9125 to 0 9160	− 8 to −16 Schädler	170 to 171	92 to 98	95 to 96	. . .
Oil from nasturtium officinale φφ	. .	1 470	0 9205	−5 to −6	170.9	98 6	102 5	. .
Oil from lupines φφ		1 475	0 920	−5 to −10	185 to 193	61 to 83	..	.....
Rice oil**	......	1.474	0.923	2	193 5	106 to 108	109 5	....
Oil from peas φφ	.....	1 4766 35°	0.919	−15	184 5	106	108.4	....

* In cottonseed stearin (pressed off from the oil) 3.3 per cent of stearic acid is present according to Hehner and Mitchell.

† Henriques, Chem. Ztg., 1894; Philippe, Moniteur Scientif., 1902, 728. Sprinckmeyer and Diedrichs, Z. Nahr. u. Genussm., 26, 86 (1913), Matthes and Holz, Arch. Pharm., 251, H. 5; Chem. Umschau, 20, 248 (1913), Besson, Chem. Zentralbl., 1914, II, 954.

‡ Wallenstein u. Fink, Chem. Ztg., 1894, 1191.

Acetyl value	Hehner value	Melting point of the fatty acids, °C.	Solidification point of fatty acids, °C.	Behavior soap solution at 20° (page 388)	Main components of oil	Reactions and other characteristics
16.6	95 9 to 96 2	34 to 38 5	32 2 to 37 6	Heavy flocculent precipitate	Linolein, olein, stearin,* palmitin	Bechi, Millіau and Halphen reactions; 1.64 per cent of a yellow unsaponifiable oil Crude oil is ruby red to almost black.
......	95	29 (36)	23 to 24	.. .	Linolenic. Linoleic 29 5 per cent. Oleic 44.5 per cent. Palmitin 26 per cent	Green color, gives Halphen reaction.
11.5	95 6 to 95 9	21 to 31 5	21 to 24	Heavy flocculent precipitate	Linolein, olein, stearin, palmitin	Baudouin reaction.
7.8 to 8 75	88 2 to 95 7	18 to 20	14 to 16		4.5 to 7.5 per cent solid fatty acids (Hopkins and others), no stearin according to Hehner and Mitchell. 1.35 to 1.55 unsaponifiable matter	Oil from first pressing pale yellow to golden, from second pressing red brown, the latter is richer in free fatty acids
......		18 to 20	13 to 14		Glycerides of oleic, palmitic, erucic and an isomer of linolic acid	Golden yellow color. The cold-pressed oil, like that of all oils from the crucifers, free from sulphur when prepared in this way.
......	94 2 to 96	26 to 28	23 to 24 16 to 17		80 per cent liquid acids, 70 per cent oleic acid, 24 per cent linolic, 6 per cent linolenic acid, 0.2 to 0.7 per cent unsaponifiable	Fairly good drying, about like poppy-seed oil
......	96 2	26 5 to 29 8	24 5 (Schadler)		Little investigated	Color green to red, according to the pressing
.... .	95 2	23 to 24	17		Little investigated	Light yellow.
6.3	95	16 to 21	11 7 to 13 6	Solid yellow white masses	Glycerides of erucic, rapic and stearic acids, 0.4 to 1 43 per cent arachidic acid	Crude oil has a peculiar odor, gives a green color with H_2SO_4(1.53) page 397.
......	95	16 to 17 9 to 10	15 to 17 6 to 8		Resembles rape oil. According to Archbutt, 1.18 per cent of arachidic and lignoceric acids	The crude oil generally contains sulphur.
......	96 7	15 to 16 12 to 13	17 9 to 10		Similar to black mustard seed oil	Sulphur cannot be detected in the cold-pressed oil.
.... .	94 3	24 to 25	21 to 22		.	Fatty acids, solid like butter.
. ...	94 5	24 to 35.5	23 to 32			Stearin separates at room temperature.
......	95 6	31 to 36	28 to 29	. .	Palmitic 20 per cent, oleic 45 per cent, isolinoleic 35 per cent	Becomes acid on standing (83 per cent free acid) due to lipase, destroyed on heating; 0.5 lecithin.
.... .	93	26 to 27	24 to 25	. . . . .	... ...	. . . .

§ High Reichert-Meissl value (4.2 to 4.4) obtained in oils from fermentation vats. Winfield obtained values as high as 9.9.

‖ Meister, Farben Ztg., **15**, Nr. 33; Oettinger and Buchta, Zeit f. angew. Chem., **1911**, 828. Keimatsu, Chem. Ztg., **1911**, 839; Matthes and Dahle, Arch. d. Pharm., **249**, 424, **1911**; Zeit. f. angew. Chem., **25**, 179 (1912).

‡‡ Grimme, Chem. Umschau, **18**, 53, 77 (1911); **19**, 102 (1912). Pharm., Cent. **52**, 141 (1911).

** Tsujimoto, Chem. Umschau, **18**, 111 (1911).

TABLE

VEGETABLE

(The less common values are placed in brackets)

Kind of oil	Engler viscosity at 20° *	Index of refraction, 20°	Specific gravity, 15°	Solidification point, °C.	Saponification value	Iodine value	
						of the oil	of the fatty acids
Poppy-seed oil, *Mohnöl*, *Huile d'oeillette*	8 0 to 8.1	1.478, 79.4 scale divisions	0 9240 to 0 9270	Generally still liquid at − 15, solid at − 18	190 to 198	134 to 143 (157.5)	139, liquid fatty acids 150
Manketti Nut oil ϕϕ	. ...	1 480	0 928 to 0 931	.	194	128 6, Wijs 134 8	136 to 138
Oil from Kickxia elastica ϕϕ	... ...	40° 68 8 25° 77 3	0 933		179 6	130 9	139 7
Manihot oil ϕϕ		40° 61 8 25° 70 2	0 924		192 5	117 6	131 6
Sunflower oil, *Sonnenblumenöl*, *Huile de soleil*	8 2	60° 1 4611	0 9240 to 0 9260 (0 9325)	Still liquid at − 12, partially solid at − 17	188 to 194	122 to 135	133 to 134 (124)
Walnut oil, *Nussöl*, *Huile de noix*	... ...	22° 1 4804	0 9250 to 0 9265	Liquid at − 15, solid at − 27 5	189 to 197	143 to 148 (152)	151, liquid fatty acids 167
Hemp-seed oil, *Hanföl*, *Huile de chênevis*	8 3	Oleo. refract. scale divisions 22° 34 to 37	0 9250 to 0 9280 (0 9310)	Liquid at − 15, solid at − 27 5	190 to 194	157 to 166	160 to 170
Linseed oil, *Leinöl*, *Huile de lin*	6 8 to 7 4	1 484 to 1 487	0 9305 to 0 9357 (0 9370)	Liquid at − 15, solid between − 16 and − 21	188 to 192 (187.6) (200 to 221)	Baltic 181 to 204, Indian 176 to 191, La Plata 171 to 186, South Russian 176 to 182, North American 177 to 188	179 to 182
Perilla oil ‡	. . . . .	15° 1 483 to 1 485	0 928 to 0 933	....	187 to 192 194 to 197	196 188 to 193 181 Wijs 206	200
Plukenetia oil §	5 6 to 6 5	15° 1 483 to 1 484	0 9354 to 0 9409	Liquid at − 15, faintly turbid, not liquid at − 21	191 to 192	177 (Kr.)–195 to 200 (H. a. M.)	187 (Kr.) 211
Tung ‖ (Chinese wood) oil, *Holzöl Tungöl*, *Huile de bois*	39	1 503 25° 1 510 to 1 520	0 9406 to 0.9440 (0.9360)	Fresh oil solidifies at + 2 or + 3, old oil is still liquid but viscous at − 18, solidifies at − 21	190 to 196 155.6 (?) 221 (?) the fatty acids 188 8	159 to 163 171	160 to 170
Japanese wood oil **	....	1 5034 to 1 5083	0.9349 to 0.9400	....	193 to 196	149 to 158	....

* Bach, Zeit f. öffentl. Chem., 1898, 168; Thoms and Fendler, Chem. Ztg., 28, Nr. 72 (1904).
† Jensen, Chem. Zentrallblatt, 1911, II. 797.
‡ Rosenthal, Farben. Ztg., 17, 739 (1912); Meister, Farben. Ztg., 16, 266; Niegemann, Farben. Ztg., 17, Nr. 6.
ϕϕ Sprinckmeyer and Diedrichs, Z. Nahr. u. Genussm., 27, 113, 120 (1914).
** Chapman, Analyst, 37, 543 (1912). Z. Nahr. u. Genussm., 25, 611 (1913).

Acetyl value	Melting point of fatty acids, °C.	Solidification point of fatty acids, °C.	Main components of the oil	Reactions and other characteristics
13 1	20 2 to 21	15 4 to 16 5	Stearin and palmitin. In the liquid fatty acids 65 per cent linoleic acid, 30 per cent oleic and 5 per cent linolenic and isolinolenic acids	Much used for making oil colors in tubes.
	39 to 41	35 to 36	No hexabromide reaction. Linoleic acid present	Much like poppy-seed, varnish dries slower than linseed oil.
.	25 2	23 0	Linoleic and linolenic acid present	Usable in varnishes.
	25 8	23 5	Linoleic, no linoleic present	R-M value 10 7, Polenske value 0 5.
.	22 to 23 (17)	17 to 18	The liquid fatty acids consist mainly of linolic and a little oleic acid	Unsaponifiable 0.3 to 0.7 per cent.
4 6	16 to 20	16	Myristic and lauric acid glycerides Liquid acids, mainly linoleic and small amounts of oleic, linolenic and isolinolenic acids	Used by artists because it drys to a good varnish, while linseed oil varnish is liable to crack.
7 5 to 20	17 to 19	15 6 to 16 6	Stearin and palmitin. Glycerides of linoleic acid, little oleic, linolenic and isolinolenic acid	5 parts oil (unrefined) shaken with 1 part of Bieber's reagent gives a green then black color.
8 5	17 to 21	19 to 20 6	0.5 to 1 5 per cent of unsaponifiable, 8 to 9 per cent satur. acids (myristic, palmitic, stearic arachidic), 15 to 20 per cent oleic, 25 to 35 per cent linoleic, 35 to 45 per cent linolenic acids 4 to 5 per cent glycerine	Cold-pressed oil (1 sample) contains 0.42 per cent, warm-pressed oil contains 0.32 to 0.92 per cent, extracted oil 0.61 to 0 92, boiled oil 0.43 to 0 74, per cent of unsaponifiable oil.* The Liebermann reaction for rosin fails with linseed oil, for rosin free oils give a color in proportion to the amount of unsaponifiable material contained.†
	− 4 to − 5		.	Has greater drying power than linseed oil. Hexabromide value up to 64 1 per cent.
	24 to 28			The same. Reichert-Meissl value 0.5 to 1. Polenske value 0.2 to 0.3. Hexabromide 47.7 per cent.
	43 8 39 to 40	31 2	Is said to consist of olein and 75 per cent elaeostearin (glyceride of the acid $C_{18}H_{32}O_2$). This α-elaeostearic acid (M.P. 48°) changes to β-elaeostearic acid (M P. 72) by action of light (Kronstein). According to Fahrion¶ contains 10 per cent oleic and only 2 to 3 per cent saturated acid	Milliau and Bechi reactions positive. Evaporated from carbon disulphide solution, a crystalline mass melting at 34°. Becomes gelatinous on boiling. Odor! No hexabromide.
. . .	. . . .	. . . .	. . . .	After ploymerization still liquid, under same conditions, tung oil is hard.

§ Krause, Tropenflanzer, **1909,** 281; Holde and Meyerheim, Chem. Ztg., **1912,** 1075. Hammelmann, Farben. Ztg., **18,** 2175 (1911).

‖ David and Holmes, Pharm. Jour., **1885,** 634, 636; Cloez, Bullet. Société Chimique, **26,** 286; Negri and Sburlati, Analyst., **1898,** 113. Hoepner and Burmeister, Chem. Ztg., **37,** 18, 39 (1913).

¶ Farben. Ztg., 1912.

TABLE

VEGETABLE OILS FROM

Kind of oil	Scale divisions on Butyro-refractometer at 40°	Specific gravity at 15°	Solidification point °C.	Saponification value	Iodine value		Reichert Meissl value
					of the oil	of the fatty acids	
Spindle tree oil, *Spindelbaumöl*, *Huile de fusain*	52	0 939	On standing oil separates into solid and liquid	Fatty acids 223 6	......	105 3	35 3
Tomato seed oil, *Tomatensamenöl*, *Huile de tomate*	63	0 920	− 9°, viscous −12° salve-like	183 6, fatty acids 199 5	117 8	129 6	0.22
Current seed oil, *Johannisbeersamenöl*, *Huile de groseille*	62	0 912	− 17.5° salve-like, though flowing	171 3, fatty acids 211	152 5	169 5	0 77
Raspberry seed oil, *Himbeerkernöl*, *Huile de framboise*	65	0 915	−17.5° salve-like, though flowing	180.3, fatty acids 203.6	162 2	170 3	0.11
Dog rose seed oil, *Hagebuttensamenöl*, *Huile des graines du rosier sauvage*	67	0 916	− 17.5° salve-like, not solid	172 8, fatty acids 202 9	152 8	174.3	0 44
Strawberry seed oil, *Erdbeersamenöl*, *Huile des graines du fraise*	65	0.934 at 60° 0.974	....	193 7, fatty acids 233.1	180 3	191 to 193 insoluble fatty acids	3 1

99

Various Seeds

Melting point of the fatty acids °C.	Solidification point of acids °C.	Behavior of the soap solution page 388	Main components of the oil	Other points
Begins 38	....	At 18 to 20° a small flocculent precipitate	Stearin, palmitin, triacetin, some benzoic acid	Yield of oil 35 per cent.
26 to 29 capillary	Solid at room temp.	The same	Stearin and palmitin	Yield from seeds 17 3 per cent; odor of tomatoes.
....	−20	No flocculent precipitate	....	Yield, 16 9 per cent mobile, yellow brown oil.
At 30° the solids melt in capillary	....	Small flocculent precipitate at 18 to 20°	Linoleic and linolenic, oleic, iso-oleic acids, phytosterin 0.7 per cent	Yield, 13.5 to 14.5 per cent.
At 31° the solids melt in capillary	....	The same	....	Yield, 9.6 per cent.
21	....	....	Linoleic and linolenic acid	Yield, 16.5 to 19 per cent yellow, viscous oil; dries like linseed oil.

TABLE

ANIMAL FATS

(The less common values are placed in brackets)

Kind of oil	Consistency at room temperature	Index of refraction	Specific gravity 15°	Solidification point, °C.	Saponification value	Iodine value: of the oil	Iodine value: of the fatty acids
Neat's-foot oil, bone fat, *Klauenfette*, *Knochenöle*, *Huile de pieds de bœuf*, *suif d'os*	Oils rich in stearin, often solid, Engler viscosity at 20° 12 0	20° 1 466 to 1 470, 60 to 66 scale divisions	0 914 to 0 916	According to the method of preparation, above or below 0	191 to 203	According to stearin content, 44 to 75 (82)	Crude bone fats 44 to 75
Horse fat *Pferdefett*,† *Graisse de cheval*	Considerable separation of stearin or entirely solid	40° 53 7 scale divisions	0 919 to 0 9220	Variable, according to Amthor and Zink, between 20 and 30, melting point 30 to 33	195 to 199	75 to 86 (71.4)	84 to 87
Beef tallow, *Rindstalg*, *Suif de bœuf*	Solid	60° 1 4510, 40° 44 to 49 scale divisions	0 943 to 0 952, 100° 0 860 to 0 861	Melting point 42.5 to 46	193 to 200	35 to 44, Australian tallow 45	41 3, liquid acids 92
Mutton tallow, *Hammeltalg*, *Suif de mouton*	Same	60° 1.4510, 40° 44 scale divisions	0.937 to 0.940, 100° 0.857 to 0 860	Melting point 46.5 to 51, solidification point 32.9 to 41.0	193 to 196	35 to 46	34 8, liquid acids 92 7
Tallow oil, *Talgöl*	Liquid to semi-solid	..	100° 0 794	34.5 to 37.5		54.6 to 57	
Lard, *Schweineschmalz*, *Sain-doux Lard*	Salve-like	40° 49.0 to 52 (45) scale divisions	0.931 to 0 938, 100° 0 858 to 0 860	27.1 to 29.9; melting point 33 to 48 generally 36 to 40	195 to 197	53 to 64, from foot 77 3, rom head 85, American 60.4 to 68 4	64 liquid acids, European 93 to 96, American 103 to 105
Lard oil, *Schmalzöl*, *Huile de Lard*	Liquid to semi-solid	40° 41 scale divisions	0 915	10	191 to 196	67 to 82 (88)	Liquid fatty acids 94 to 95.8
Butter fat, *Butterfett*, § *Beurre de vache*	Salve-like	40° 41.6 to 44 2 (46) Margarines 58.6 to 66.4 scale divisions	0 936 to 0 946 100° 0.864 to 0 868	19 to 20, melts at 29.5 to 34.7	209 to 240	26 to 38 9	28 to 31

* Fahrion, Zeit. f. angew. Chem., **1911**, 209.

† Amthor and Zink, Frühling, Zeit. f. angew. Chem., **1896**, 352; Nussberger, Zeit. f. anal. Chem., **1897**, 269; values are for fat from back, kidneys, heart and neck.

‡ The fat from the breast and legs contains no stearic acid.

§ Büffelbutter from Macedonia is like cows' butter, Jorissen (Chem. Ztg., **1898**, 162) 0.866 at 100°, refractive index 45, Reichert-Meissl value 29.6.

100

AND OILS

Reichert-Meissl value	Acetyl value	Hehner value	Melting point of the fatty acids, °C.	Solidification point of the fatty acids, °C.	Main components of the oil or fat	Reactions and other characteristics.
0 (Duyk)	11 3	92 to 96	Varies according to method of preparation and stearin content, American oil 29.8 to 30 8 13 to 37*	Varies according to stearin content 26 1 to 26 5	Olein, stearin, free oleic and stearic acids	Generally recognized by its peculiar odor.
1.6 to 2.2 (Kalmann), 0 4 to 0 8 (Amthor and Zink)	1 8 to 2 4 (6 to 14)	96 to 97 8	36 to 42	30 to 38 6 33 6 to 33 7	Olein, stearin and free oleic and stearic acids	Yellow color. Fat from neck half liquid at 15°.
0.25 to 0.5	2 7 to 8 6	95 to 96	43 to 47	37 9 to 46 3	Palmitin, stearin and olein, mixed glycerides, 50.6 per cent stearic acid according to Hehner and Mitchell	By pressing (also of tallow) is obtained oleomargarine. Used in manufacture of oleomargarine.
....		95 5	46 to 54	43 to 46	Olein, stearin, palmitin, mixed glycerides, 16.4 to 27.7 per cent stearic acid according to Hehner and Mitchell‡	Gets rancid more easily than beef tallow.
.... .					Olein	Obtained by pressing tallow.
0.3 to 0 9	2 6	93 to 98	35 to 47	34 to 42	Palmitin, stearin 62 per cent (?) olein, mixed glycerides	Solidifies with crystalline surface. Can be distinguished from tallow microscopically.
0	. .	. .	..		Olein	Obtained by pressing of lard. Test with nitric acid and elaidin test similar to olive oil.
26 to 33 ||	1 9 to 8 6	86 to 88	38 to 45	35 8 to 38	Butyrin, caproin, caprylin, laurin, palmitin, stearin, etc.¶ Rancid butter contains (Amthor) ethyl esters of butyric acid and other volatile esters	Cheese fat has constants similar to those of butter fat.

|| 22.7 to 24.2, Farnsteiner and Karsch (in exceptional cases). Butter under 26 is to be suspected. Addition of cocoanut oil, see page 346, Polenske value. Juckenack and Pasternack, Zeit. f. Unt. d. Nahr. und Genussm., **1904**, 193.

¶ Bell (Chemistry of Foods, 44), confirmed by Blyth and Robertson, assumes the presence in butter of an oleo-palmito-butyrin.

TABLE

FATS AND OILS FROM

(The less common values are placed in brackets)

Kind of oil		Specific gravity, 15°	Solidification point, °C.	Saponification value	Iodine value of the oil	Iodine value of the fatty acids	Reichert-Meissl value
Seal oil, *Robbentrane*, *Huile de phoque*		0 925 to 0 926	−2 to − 3	189 to 196 (178 to 179)	127 to 152 (162 6)*	Liquid acids 307 (Bull)	0.07 to 0.44
Whale oil, *Walfischtran*, *Huile de baleine*		0 917 to 0 927	Crystalline separation at + 10 (Schädler)	Southern oil 188 to 193, Northern oil 188 to 224	110 to 128, 136 Southern	130 to 132, liquid acids 145	0 7 to 2 4
Dolphin (black fish) oil, *Delphintran*, *Huile de Dauphin*	From the entire body	0.928 to 0 930	Crystals separate from + 5 to − 3	197.3 to 203.4 217 to 230	99.5 to 128.3 114 to 125	. ...	5.6 30 to 44
	From the soft fat from head and jaws	0.925	−16	290 280	32 8 24 5	.	65 9 112
Porpoise oil, *Meerschweintran*, *Huile de Marsouin*	From the entire body	0 926 to 0 937	−16 (Schädler)	216 to 218.8 (195)	119 4	.. ...	11 to 12 (23)‡
	From head and jaws	0 9258	....	Freed from solid particles by filtration and 253 to 272	40 to 50		48 to 66
			.....	Not pressed and clarified 144	77		2 08
Menhaden oil, *Menhadentran*, *Huile de Menhaden*		0 9311	− 4 (Jean)	189 to 192	148 to 160	.. .	1 2
Sardine oil, *Sardinenöl*, *Huile de Sardine*		0 9330	....	Ordinary sardine oil	193	....	......
		0 916 to 0 934	....	Japanese oil 189 to 192	100 to 164	......	......
Cod liver oil, *Dorschlebertran*, *Huile de foie de morue*		0 922 to 0 941	According to origin partially solid at 0, or liquid at − 10	171 to 193	135 to 168 (181)	164 9 to 170 (130)	0.2 to 2 1

* Thomson and Dunlop, Oil and Colourm. Journ., **29**, No. 392.
† Tsujimoto, Chem. Umschau., **16**, 84 (1909); **20**, 70 (1913).
‡ Steenbuch, Zeit. f. angew. Chem., **1889**, 64.
§ In the specially prepared Japanese oil Fahrion could find no jecoric acid, but he found the liquid unsaturated asellic acid. Lewkowitsch considers the question of the composition of the fish oils still open (see Weiss, Der Gerber, **1893**, 137).

101
MARINE ANIMALS

Hehner value	Melting point of the fatty acids, °C.	Solidification point of the fatty acids, °C.	Main components of the oil	Other properties
92.8 to 95.5	22 to 23	15 5 to 15 9	83 to 89 per cent liquid and 9.8 to 17 per cent solid fatty acids. Mostly glycerides. Physetoleic and oleic acids according to Ljubarsky. The odor is caused, like that of all fish oils, by unsaturated acids, clupanodonic acid ($C_{18}H_{28}O_2$) and homologues† also amines	Yellow to dark brown color. According to Douzard the refractive index of seal oil is 32 to 32.5 scale divisions, of cod-liver oil 43.5 to 45. (Determined with Jean Amagat refractometer)
93 5	14 to 27	22 9 to 23 9	Mostly glycerides of liquid fatty acids. Solid crystals, mainly palmitin and some sperm oil. Clupanodonic acid, see seal oil	Color generally brown, 0.7 to 1.4 per cent of unsaponifiable matter, in light-colored refined oil 0.9 to 3.7 per cent.
93 1		...	Glycerides of solid and liquid acids and valerianic acid with some sperm oil. Clupanodonic acid, see seal oil	Color pale yellow. On standing cetyl palmitate separates.
66.3	.	..	The same, with more of the triglyceride of valerianic acid	Color, straw yellow.
.	......	....	Glycerides of oleic, physetoleic (?), stearic, palmitic, valerianic acids. Clupanodonic acid, see seal oil	Pale yellow to brown color. An easily soluble oil can be extracted with alcohol.
pressing 68 to 72 96 5	....	... .	As above, only content of valerianic acid greater	Easily soluble at +70° in alcohol.
....	...	.....	Mainly glycerides of liquid fatty acids, clupanodonic acid	Brown color, oil easily absorbs oxygen. Contains 0.6 to 1.6 per cent of unsaponifiable components.
94 5 95 5 to 97	....	... 27 6 to 28 2	Solid glycerides, according to Fahrion, mainly palmitin, little stearin, liquid acids. Jecoric acids,§ 85.7 per cent trijecorin, 14.3 per cent tripalmatin. Clupanodonic acid, see seal oil	Brought on market from Japan. Generally 0.6 unsaponifiable in the common, 0.5 to 1 4 per cent in Japanese oil.
95.3 to 96 5	Of the solid acids 21 to 25	13 3 to 24.3	87 to 97 7 per cent liquid and 5 3 to 12.8 per cent of solid fatty acids, a complicated mixture. Small amounts of palmitin and stearin. Liquid acids not sufficiently investigated ‖ according to Heyerdahl 20 per cent of jecoleic and 20 per cent of therapic acid. Bull (Chem. Ztg., **1899**, 996) suggests a fractional separation of the alkali salts of the liquid acids. Clupanodonic acid, see seal oil	Brown. 0 02 to 0 03 per cent iodine and 0 3 to 1 3 per cent of cholesterin. 2 7 per cent of unsaponifiable (generally not over 1.5 per cent). Free fatty acids 3.8 to 28 per cent. Giving with nitric acid (sp. gr. 1.53) a red color at zone of contact, a fiery red on stirring, a lemon yellow after a short time.¶

‖ Fahrion (Chem. Ztg., **1893**) assumes the presence in the liquid acids of asellic acid $C_{17}H_{32}O_2$; the iodine value of the liquid acid is 175.5. Meigen, Chem. Umschau., **24**, 34, 35, (1917).

¶ Merlangus oil and Japanese fish oil give at the point of contact an intensive blue brown on stirring; on 2 to 3 hours standing, the mixture will be yellow. With seal oil the color at first is unchanged, later it becomes brown.

CHAPTER VII

INDUSTRIAL PRODUCTS PREPARED FROM FATS

A. Hardened Oils

I. General

In the last few decades many attempts were made to change liquid oils into the more costly solid fats and fatty acids; until 1902, when Normann was able to catalytically hydrogenate neutral fats and fatty acids, most of the experiments were concerned with fatty acids. Heating oleic acid with zinc chloride* produced a material containing 75.8 per cent of stearolactone, 15.7 per cent of iso-oleic acid and 8.5 per cent of saturated fatty acid; another method consisted in changing oleic acid into palmitic acid by fusion with alkali, but the yield was unsatisfactory.

Success came with the application to the problem of the Sabatier and Senderens method of catalytic hydrogenation.† Hydrogen is added to oleic, linoleic, linolenic, and clupanodonic acids with the aid of finely divided contact materials (nickel) as follows: —

$$\text{oleic acid } (C_{18}H_{34}O_2) + \text{hydrogen } (H_2) \rightarrow \text{stearic acid } (C_{18}H_{36}O_2)$$
$$\text{triolein } (C_3H_5(C_{18}H_{33}O_2)_3) + 3\ H_2 \rightarrow \text{tristearin } (C_3H_5(C_{18}H_{35}O_2)_3)$$

The change of liquid fatty acids and their glycerides into solid products is accomplished industrially by means of nickel obtained by reduction of nickel oxide; the action is improved by spreading the contact material over diatomaceous earth.‡ Nickel oxide§ is also recommended and is said to produce a catalytic material which is less sensitive to " poisons " than metallic nickel. Normann|| claims, however, that only chemically pure oxide catalyzers are more active than the metallic nickel itself; the latter has been found to be more active

* Monatshefte, **11**, 90 (1890).

† Fahrion, Die H rtung der Fette, Braunschweig, 1915. Klimont, Die Neuren Synthetischen Verfahren der Fettindustrie, Leipzig, 1916. Ellis, Hydrogenation of Oils, Van Nostrand, New York.

‡ D. R. P. 141029. U. S. Patents 1004034; 1008474; 1004035; 1001279.

§ D. R. P. 292649.

|| Chem. Ztg., **40**, 757 (1916).

on an industrial scale, its sensitiveness to impurities having been exaggerated. Other nickel derivatives have been suggested: nickel carbonate, nickel carbonyl, nickel formate and lactate, and nickel borate. The oxide and nickel salts probably are all transformed by the hydrogenation into metallic nickel,* which is the active catalyst.

Ellis considers the use of oxide a disadvantage as fatty acids in the oils may produce nickel soaps which are poisonous; metallic nickel does not react with such free acids. The temperature necessary for the reduction of the oxide and salt catalysts (200 to 250° C.) is higher than the temperature at which nickel metal is used (180° C.); this may affect the taste of oils intended for edible purposes.

The nickel catalyst is emulsified with the oil and brought in contact with the hydrogen in an autoclave at a temperature ranging from 100 to 160° and with a hydrogen pressure of about 9 atmospheres.

Besides nickel and its compounds, which are used in considerable concentration (0.5 to 1 per cent) in the reduction, colloidal platinum (Fokin, Willstätter) and palladium (Paal) may be used in the laboratory experiments. Palladium is indeed used industrially to some extent in amounts as small† as $\frac{1}{50000}$ to $\frac{1}{100000}$ of the amount of fat; palladium chloride (with rubber or gelatine as a protecting colloid) is used.

II. Properties

Liquid oils are converted into more or less hard products according to the degree of hydrogenation; the softer products resemble lard in odor and taste, the hard materials are like beef and mutton tallow. The melting point and the density rise, while the iodine value, solubility in ether, and the index of refraction, drop as the degree of hydrogenation increases. The addition of hydrogen also causes a considerable bleaching and deodorization of raw material (as fish oils); the hardened oils do not easily become rancid, and certainly have less tendency to do so than the unhardened oils.

Table 104 gives the analytical data determined for oils completely hydrogenated at 100° by means of palladium spread over carbon.‡

* J. Prakt. Chem., **87**, 425 (1913); **89**, 290 (1914); **91**, 442469 (1915); **92**, 390 (1915). Z. angew. Chem., **28**, 365 (1915). Chem. Ztg., **39**, 29, 41 (1915); **40**, 381, 757 (1916). Arch. der Pharm., **253**, 512 to 573 (1916).

† D. R. P. 230724.

‡ Ber. d. Pharm. Ges.. **26**, 36 (1916).

TABLE 103

HARDENED OILS

Trade name	Source	Solidification point, °C.	Melting point, °C.	Iodine value	Saponification value	Acid value
Tallow oil.....	Fish oil	31	35 to 40	60 to 70	191	3.4
Tallow oil..... (extra)	Fish oil	38	42 to 45	35 to 55	191.3	3.5
Candelite......	Fish oil	42	48 to 50	15 to 20	191.0	3.2
Candelite...... (extra)	Fish oil	45	50 to 52	4 to 15	190.8	3.9
Divintol.......	Cocoanut oil	....	60	4 to 5	161.6	...
Coryphal......	Castor oil	....	81	18 to 20	189.9	3.3

TABLE 104

PALLADIUM HARDENED FATS

Material	Melting point	Iodine value	Saponification value	Index of refraction	Melting point of fatty acids
Olive oil	.....	83.8	190 9	62.2(25°)	....
Olive oil hardened......	70	0.2	190.9	...	71
Almond oil	......	99.1	193.7	65.3	....
Almond oil hardened....	72	0.0	191.8	...	71
Peanut oil	....	93.5	193 0	64.9	....
Peanut oil hardened....	64 to 64.5	0.0	191.6	...	67
Sesame oil	...	99.9	190 2	66 3	....
Sesame oil hardened....	68.5	0.7	190.6	.	69 5
Cocoa butter.........	31	36.5	194 5	46.5(40°)	......
Cocoa butter hardened.	63.5 to 64	0.0	193.9	...	65.3
Poppyseed oil....	...	139.0	193.2	72.0(25°)	....
Poppyseed oil hardened	70.5	0.3	191.3	....	71
Linseed oil....	.....	168.1	191.8	79.1	......
Linseed oil hardened....	68	0.2	189.6	..	70.5
Tallow...	51	36.7	197.6	46.2(40°)	....
Tallow hardened.......	62	0.1	197.7	...	64
Lard...	36	48.4	197.5	49.5	....
Lard hardened.........	64	1.0	196.8		62
Cod liver oil	....	158.9	187.3	77.0(25°)	....
Cod liver oil hardened...	63	1.2	186.2	......	59

It has not yet been determined whether the hydrogenation of the most unsaturated acids proceeds by stages. Marcusson and Meyerheim* found that "Talgol" had an iodine value of 64.8 and an inner iodine value of 107, from which it follows that a part of the most unsaturated acids remains unsaturated even when the less unsaturated oleic acid has already been changed to stearic acid.

* Z. angewandte Chem., **27**, 201 (1914).

When castor oil is reduced* at 200° only the unsaturated double bonds are attacked; above 200° however, the hydroxyl groups react (in presence of oxide of nickel, even more rapidly than the double bonds). At 200° a fat of melting point 81° and hydroxyl value 100 to 165 is obtained; treated at 250°, the product gives an hydroxyl value of only 31. Rincinoleic acid is not attacked at 150°, at 250° the hydroxyl groups react easily.

Hardened oils are used in the soap industry and have been found satisfactory when properly mixed with other soap-stock. When first introduced the lathering power of the soaps produced was not satisfactory. It is claimed that hardened oils have not been found entirely satisfactory in the manufacture of candles. In the production of edible fats, it is important that no nickel remain in the fat. This is said to occur only when the oil hardened contained free fatty acid. A sesame oil with 2.58 per cent of free fatty acid gave in the hardened oil only 0.006 per cent of nickel oxide; with 0.61 per cent of free acid in a blubber oil, 0.0045 per cent of Ni_2O_3 was found. With 0.2 per cent of free acid in the oil, nickel could not be detected in the hardened product. From 0.02 to 0.20 milligram of nickel was found in 1 kilogram of hardened cottonseed oil; hardened palm oil contained from 0.02 to 0.15 milligram per kilogram of fat. These quantities are presumed to be harmless.†

III. Tests

(*a*) **Melting Point and Iodine Value.** The fats are graded according to their melting points and iodine values. See Tables 103 and 104.

(*b*) **Color Reactions.** The Halphen reaction for cottonseed oil is not given by the hardened product;‡ the Baudouin test is still given by hardened sesame oil. The Beechi test is given by slightly hardened cottonseed oil, but less definitely by harder products; if given it points to cottonseed oil, if not given, cottonseed oil may still have been used.§

The inner iodine value is of importance in testing for train oil but the other tests given on page 392 are not very definite.||

The bromine reaction (page 393) does not detect hardened fish oils. Arachidic and behenic acids are present up to 20 per cent, therefore the

* Chem. Umschau., **23**, 99, 116 (1916).

† Z. Nahr. -u. Genussm., **24**, 104 (1912). Chem. Umschau, **20**, 250 (1913). Chem. Ztg., **38**, 796 (1914). Siefensiederztg., **42**, 890 (1915).

‡ Z. Nahr. -u. Genussm., **24**, Heft 1 and 2 (1912).

§ Chem. Ztg., **37**, 815 (1913).

|| Chem. Umschau, 20, 129 (1913). Z. angewandte Chem., **27**, 201 (1914).

Kreis and Roth method for the detection of hardened peanut oil (page 388) may be applied to fish and rape oils; if the melting point after the third crystallization is over 70°, then hardened peanut oil, or fish oil, or rape oil is under examination.

(*c*) Cholesterin and phytosterin are not attacked by the hydrogenation at low temperatures; the sterins separated from hardened vegetable oils gave the characteristic tests for phytosterin and its acetate. By treatment at 200° about 75 per cent of the cholesterin resinifies; hydrogenation at 250° gives a product which no longer yields crystalline derivatives of cholesterin which can be precipitated with digitonin. Hydrogenation at 200° does not attack phytosterin; at 250° there is formed an hydrocarbon, melting at 102 to 103° with a dextrorotatory power of + 48°, both the double bonds and the hydroxyl group of phytosterin being reduced.

(*d*) **Detection of Nickel.** 5 to 10 grams of fat are warmed ½ hour on a water bath with an equal volume of concentrated hydrochloric acid, shaking frequently; after filtering through a moistened filter, the filtrate is evaporated in a porcelain dish. The residue gives, when nickel is present, on touching with a drop of 1 per cent alcoholic dimethylglyoxime solution, a red coloration, which becomes even more noticeable on adding some ammonium hydroxide. If the acid extract is itself colored it must first be boiled with animal charcoal and then filtered.*

It must not be assumed if nickel is absent that the fat was not hardened; palladium or other catalysts may have been used.

B. Products of the Stearic Acid Industry

I. General

Beef and mutton tallows (especially the press-tallow resulting from margarine manufacture), palm and bone oils, recently also vegetable fats, such as malabar tallow, illipe-tallow, chinese tallow and shea butter, as well as hardened oils (page 439), are used in the manufacture of stearic acid candles. The raw materials, purified by melting, are decomposed in the candle manufactories into solid fatty acids or " stearine " (which consist almost entirely of palmitic and stearic acids, the candle material), liquid acids (" olein ") and glycerine.

The splitting is brought about:

(*a*) By heating with water in the presence of 1 to 3 per cent of quicklime, or small amounts of magnesia, or of zinc oxide (autoclave process) under 6 to 10 atmospheres pressure.

* Chem. Ztg., **36**, 1461 (1912); **37**, 773 (1913).

(*b*) By treatment with 4 to 12 per cent conc. sulphuric acid at 120°. Not only does saponification of the fat take place, but also some new solid acids are formed from the oleic acid; the sulphuric acid forms an ester of an oxy-stearic acid by addition to oleic acid, which is changed by boiling with water into oxy-stearic acid and sulphuric acid.

$$C_{17}H_{33} \cdot COOH + H_2SO_4 \rightarrow C_{17}H_{34}(COOH)\ (O \cdot SO_2 \cdot OH).$$
$$C_{17}H_{34}(COOH)\ (O \cdot SO_2 \cdot OH) + H_2O \rightarrow C_{17}H_{34}(OH)\ (COOH) + H_2SO_4.$$

In the steam distillation which follows, the oxy-stearic acid passes into iso-oleic acid, water being split off. This acid has the melting point 44 to 45°. The yield of solid acids obtained from palm oil is on the average 18 per cent; with tallow 14 to 15; with bone oil, 15 per cent.

The processes (*a*) and (*b*) are often united, in that after the autoclave splitting, the material is further treated with sulphuric acid to increase the content of solid acids.

(*c*) By heating with water at pressures of 15 to 18 atmospheres; this method is not much used now.

(*d*) By action of the Twitchell reagent. This is obtained by the action of excess sulphuric acid on a solution of oleic acid in aromatic hydrocarbons. Because of the good emulsions which the sulphuric ester of oxy-stearic acid and the aromatic sulphonic acids form with the fat in the presence of water, the fat is very rapidly hydrolyzed.* The formulas given by Twitchell to the products formed have not been established.

$$C_6H_4\begin{cases}SO_3H\\C_{18}H_{35}O_2\end{cases} \qquad\qquad C_{10}H_6\begin{cases}SO_3H\\C_{18}H_{35}O_2\end{cases}$$

Benzol stearo-sulphonic acid — Naphthalene stearo-sulphonic acid

Similar fat-splitting properties are said to be possessed† by a material obtained by the action of concentrated sulphuric acid on naphthalene and castor oil hardened with palladium. Sulphonated hydrocarbon oils have also been found useful.

(*e*) Fermentative Decomposition. An enzyme present in the castor bean can hydrolyze emulsified fats into fatty acids‡ and glycerine. Three layers are obtained, an under aqueous layer of glycerine, a middle

* Z. angew. Chem., **25**, 812 (1912).

† Steffan, Davidsohn, König. Seifensiederztg., **40**, 550, 1167 (1913); **41**, 311 (1914). Chem. Ztg., **39**, 329 (1915).

‡ Connstein, Hoyer and Wartenburg, Ber., **35**, 988 (1902).

layer of bits of seed and emulsified oil and glycerine and an upper clear layer of fatty acid; by using 6 to 7 parts of ferment to 100 parts of fat, after 1 to 2 days at 40 to 50°, 90 per cent will have been split. Very light-colored fatty acids and glycerine are obtained. Because the separation of the middle layer and the removal of the fat from it requires much time, and since the glycerine contains interfering impurities, the method is less used on a large scale than in smaller establishments.

(*f*) In the Krebitz process, the fats are saponified with lime; the calcium soaps are leached free from glycerine in high towers and then changed into sodium soaps and calcium carbonate by sodium carbonate solution.

The stearic acid prepared by method (*a*) is so pure, if pure fats are used, that by pressing first at low temperatures, and then at higher, to remove the liquid acids, a pure white candle material is obtained at once ("saponification stearine"). This consists mainly of stearic and palmitic acids besides a small amount of oleic acid which was not pressed off (iodine value only a few units). The liquid acid running from the presses is known as "saponification olein."

The products of processes (*b*) and (*d*) are known as "distillation stearine" and "distillation olein" since the crude materials first obtained are generally too dark and must be distilled with superheated steam before pressing. Because of its content of iso-oleic acid, "distillation stearine" has a lower melting point than "saponification stearine" but a higher iodine value, generally 15 to 30 (pure iso-oleic acid has an iodine value of 90). See page 445. According to Lewkowitsch* "distillation stearine" has the solidification point 54°, iodine value 15 to 30; while "saponification stearine" has the solidification value 55.6 to 56.7° and an iodine value of only a few units.

II. Examination of the Fat

The moisture and non-fatty materials should be determined (pages 71 and 385), as well as the solidification point of the fatty acids and less frequently, free acid, Hehner value and amount of glycerine contained.

(*a*) **The Solidification Point** is determined according to page 36 or 383, the yield of candle material depending on it. The fatty acids of the most important fats have the following solidification points.

* Analysis, II, 627, 644.

Fatty acids from	Solidification point, °C.
Beef tallow	38 to 46
Mutton tallow	41 to 48
Bone fat	36 to 42
Palm fat	36 to 45
Chinese tallow	45 to 53

(*b*) **The Content of Free and Combined Acid** is to be determined by the method of page 69; from this the yield of fatty acids and glycerine, as well as the amount of lime and magnesia, or sulphuric acid, or of Twitchell's reagent, is determined. Palm oil often contains nearly 100 per cent of fatty acid.

(*c*) **The Oleic Acid Content** is to be calculated from the iodine value (pure oleic acid, iodine value 90.1); the lower the iodine value, the more suitable the material for candle manufacture.

(*d*) **Glycerine.** For the determination of glycerine a large number of methods have been developed.

Approximate Method. Since in the saponification by potash 3 molecular weights of potassium hydroxide set free 1 molecular weight of glycerine, 168.33 grams of KOH are equivalent to 92.08 grams of glycerine, or 1 gram of KOH is equivalent to 0.54702 gram of glycerine. If the ester value of a fat is due to triglycerides, and if waxes and lactones are absent, the amount of glycerine can be calculated from the ester value. If the ester value (the milligrams of KOH necessary to saponify 1 gram of neutral fat) be "*a*," then the weight of glycerine from 100 grams fat will be (*a*) (0.054702).

For more exact methods see page 453.

(*e*) **Adulterations** are detected in the raw materials by use of the Tables 96 to 101. Adulterations of tallow and bone fat are cocoanut oil, palm nut oil, cottonseed stearin, distilled wool-fat stearine, rosin, paraffin, ceresine and carnauba wax.

	Saponification value	Iodine value	Reichert-Meissl
Tallow	192 to 200	35 to 46	....
Bone fat	191 to 203	46 to 56	....
Cocoanut oil	246 to 268	8 to 10	7 to 8.4
Palm nut oil	242 to 255	10 to 17.5	5 to 6.8

Cottonseed stearin is detected by the Halphen and the nitric acid tests (page 395), distilled wool-fat stearine by the Liebermann and

Hager-Salkowski test, rosin by the Morawski test, vegetable fats by the phytosterin acetate test (page 398). Palm oil is rarely adulterated; added palm nut oil would lower the iodine value but raise the saponification and Reichert-Meissl values. In the presence of carnauba wax, higher alcohols can be extracted from the unsaponifiable matter with acetic anhydride. Paraffin and ceresine are detected in the unsaponifiable material.

III. Amount Hydrolyzed

1. If the kind of fat is known, the amount split may be directly calculated from the acid value. With a pure cottonseed oil (neutralization value of the fatty acids equals 204) an acid value of 187.6 corresponds to 91.96 per cent hydrolyzed.

$$204 : 100 :: 187.6 : X$$

The rest (8.04 per cent) is neutral fat.

2. If the origin of the fat is unknown 2 grams of the decomposed material in 20 c.c. of absolute alcohol are titrated with $\frac{N}{2}$ alcoholic potash in the presence of phenolphthalein. Then enough alkali is run in to make up 25 c.c. altogether, the mixture is heated under a reflux condenser for $\frac{1}{2}$ hour, and the excess of alkali determined with $\frac{N}{2}$ HCl.

Example: 14.1 c.c. of KOH are used to titrate the free acids; 10.9 c.c. of KOH are then run in, the mixture heated under a reflux condenser, then titrated back with 10.2 c.c. of $\frac{N}{2}$ HCl (25 c.c. KOH neutralize 26.5 c.c. of $\frac{N}{2}$ HCl). Therefore $26.5 - 10.2 = 16.3$ c.c. were used in terms of HCl for saponification, while 14.1 c.c. of KOH equivalent to 14.9 c.c. of $\frac{N}{2}$ HCl were used to neutralize the free acid. The per cent split is:

$$16.3 : 100 :: 14.9 : X \qquad X = 91.6 \text{ per cent.}$$

In this method it is assumed that the fat contains no unsaponifiable components; if such are present, they must be determined by the method of Spitz and Hönig (page 197) and considered.

IV. Examination of the Candle Material

The finished candle material is examined for melting point (in capillary tube), solidification point (see page 383), content of neutral fat, and if of uncertain source of supply, for carnauba wax, paraffin,

ceresine, etc. Neutral fat may be present, because of incomplete saponification, or because it was added deliberately; it is determined most accurately by neutralization of the ether-alcohol solution of the fat with $\frac{N}{10}$ alcoholic sodium hydroxide, adding water till the lower layer is 50 per cent alcoholic and then extracting with low boiling naphtha by the method of Spitz and Hönig Carnauba wax raises the melting point of the stearic acid; the presence of this or other waxes is easily determined by separation and characterization of the higher alcohols. Paraffin and ceres ne are easily detected by the qualitative saponification test. Regarding the ratio of stearic to palmitic acids, which is of importance for the structure of the candle, the melting point (page 36) and molecular weight determination (stearic acid 284 and palmitic acid 256) will give information.

V. Testing of Commercial Oleic Acids

The " oleins " obtained from fats are yellow to dark brown, clear or turbid oils consisting mainly of oleic acid, in some part of strongly unsaturated acids, varying amounts of solid fatty acids, neutral fat and lactones. The following* are commercial distinctions: " saponification olein " is obtained from light-colored tallow acids and bleached palm oil, split either in the autoclave, fermentation or Twitchell process; this " olein " is free from hydrocarbons but contains considerable amounts of neutral fat. " Distillation olein " obtained by the sulphuric acid or mixed process, or from dark acids by the autoclave method and then distilled, is free from neutral fat but contains iso-oleic acid, oxy-acids, lactones and unsaponifiable matter. The so-called " white olein " is a re-distilled product of dark yellow or yellow white color, free from neutral fat and hydrocarbons. Oleins pressed from tallow, bone fat and palm fat have an inner iodine value of about 90, while cottonseed olein has an iodine value of 110 to 112.

The oleins are used as soap stock and to oil wool for spinning, as well as for the preparation of water-soluble oils.

Their examination includes the determination of the amount of neutral fat contained and of hydrocarbons and, in some cases, the amount of fatty acids.

1. **Hydrocarbons.** The qualitative test (page 76) often fails when the amount of unsaponifiable matter is very small, since the natural unsaponifiable substances are very unsaturated and decidedly soluble in alcoholic soap solution. Up to 10 per cent of unsaponifiable matter may be present in " oleins." Small amounts of

* Rosauer, Chem. Rev., **18**, 28 (1911).

TABLE

SPECIFICATIONS FOR TALLOW

Material	State	External appearance	Specific gravity at 15°
Beef tallow	Prussia, 1907	Yellow white, fresh, no rancid odor	....
	Bavaria, 1900	Quite solid, yellow white, almost odorless	0 930 to 0.940
	Saxony, 1902	....	. .. .
	Württemberg, 1904	Solid, clear, as white as possible, almost tasteless and odorless	0 943 to 0 953
	Baden, 1910		. . . ..
	Imperial Territory, 1912	White, fresh odor, not rancid, not granular	... .
Candles	Prussia, 1903	Pure white, smooth and shiny, not crumbly or greasy	....
	Saxony, 1902	Pure white, smooth, shiny, not scaly	....
	Württemberg, 1904	White, shiny, hard	1.000 at 11° (?)
	Baden, 1910	White, shiny, hard at ordinary temperatures	....

105

AND CANDLES IN FORCE, 1913

Melting point, °C.	Solidification point, °C.	Acid value, per cent oleic acid	Other properties
....	33 to 40	At most 7	Free from mineral acid, foreign admixtures, skin and flesh particles, soluble clear in ether without residue.
Over 45	Over 38	At most 2 45	From the purest beef fat, no added components, mechanical impurities not more than 0.5 per cent.
.... .	.	Free from acid	(Russian) pure, free from foreign material, clear when melted.
Over 42	Over 37	At most 3 0	Pure beef fat, free from other fats and other components, not more than 1 per cent impurities, no scum or foam on heating, or odor or sediment. In boiling alcohol (sp. gr. 0 822) or ether, completely soluble.
	Over 37, fatty acids over 43.5	At most 1 4	Pure beef fat, free from other fats, foreign bodies and mineral tallow. Not more than 1 per cent impurities. Completely soluble in boiling alcohol or ether.
40		Not more than 2 per cent calculated as oleic acid	Beef tallow, free from mineral acid, alkalies and skin, unadulterated, soluble in ether.
Over 52	....	Free from oleic acid	Stearine candles of definite dimensions, giving a clear sound on hitting together. Free from neutral fat (tallow, cocoanut oil, etc.), and paraffin, burning brightly, without soot, without dripping., Wick uniform and firm.
....	....		Pure stearine free from tallow, paraffin, etc., giving a clear, hard sound on hitting together, not breaking easily. Wick uniformly firm, burning brightly without soot, the wick crooking slightly; no ash or carbon on the glowing tip. The candle should not drip, nor should it smoulder after extinguishing. Length without tip 120 mm., diameter 26 mm.
Over 53	....	....	From stearic acid, free from admixture, paraffin and tallow not more than 1 per cent; wick in middle, uniformly strong, not needing cleaning. Paper rubbed over the surface of the candle should not become greasy.
....	....	....	

such hydrocarbons are determined with certainty by the saponification of about 20 grams of "olein" and extraction of the soap with petroleum ether (page 197); in this way products which resemble mineral oil are obtained; they are often partially solid because of the separation of paraffin. These products are distinguished from added mineral oil by their strong iodine absorption (iodine value 62 to 69), optical rotatory power (α_D = + 4.8° to + 9.6°) and color reaction on treating with acetic anhydride and sulphuric acid.*

Marcusson has also elaborated the qualitative method of Holde for detecting mineral oil, into one for distinguishing the natural hydrocarbons of the "oleins" from added mineral oil. 6 to 8 drops of oil are boiled for two minutes with 5 c.c. $\frac{N}{2}$ alcoholic potash in a test tube; then 15 c.c. water are added. If a pure "olein" is being tested heavy type can be seen through the faint turbidity; with oil adulterated with mineral oil or rosin oil, such type is no longer legible.

2. Neutral Fat. (*a*) *Qualitative Test.* 2 c.c. of "olein" are dissolved in about 6 c.c. of absolute alcohol by warming, then 1 to 2 c.c. of dilute ammonia are added. A turbidity indicates neutral fat, provided that this disappears on boiling with $\frac{N}{2}$ KOH; if the turbidity does not disappear on heating with KOH, mineral oil is probably present.

(*b*) *Quantitative Test.* The amount of neutral fat can be estimated only approximately from the ester value, because this is the sum of neutral fat (glycerides) and lactones (internal anhydrides). A knowledge of this quantity is useful industrially, as usually in the textile industry it is important to know the amount of fatty acid which can be washed out with soda. If the true amount of glycerides is to be determined, the glycerine is determined by the bichromate method (page 455); however this is usually in error to the extent of 1 per cent. The difference in the ester value and the amount of glyceride determined by the glycerine content gives a measure of the amount of lactones contained.

3. **Saponifiability.** The amount of saponifiable material can be calculated from the saponification value (see page 197) assuming the equivalent weight of olein to be 200. This is true only when dealing with an "olein" and not with fatty acids, such as are obtained from fish oil and sold as "olein."

4. Solid fatty acids are determined by the method of Varrentrapp (page 371).

5. Highly unsaturated liquid acids which make an "olein" unsuitable as a material for oiling wool are detected by their high iodine value (also see page 374); the iodine value of normal "distillation olein" and "saponification olein" does not rise over 85. "Oleins from wool fat" see page 521.

* Chem. Umschau, **12**, 2 (1905).

C. Glycerol (Glycerine)

I. General

Glycerine, which is present as glycerol ester in all saponifiable fats and oils, is a by-product of stearic acid and of soap manufacture; glycerine also occurs as lecithin as in the brain. In the industries, dilute glycerine solutions are obtained; these may contain varying amounts (from 5 to 20 per cent) of glycerol. By suitable treatment and evaporation crude glycerines are obtained; these crude glycerines are distinguished according to their origin (soap-lye glycerine, autoclave glycerine, Twitchell, fermentation, Krebitz). The crude glycerines may be refined by chemical treatment and by decolorization; distilled glycerine is obtained by the distillation of crude glycerines.

Glycerine is also obtained by the fermentation of sugar, usually in small amounts, but if the yeast is grown in the presence of sodium bisulphite, very considerable yields are possible.

In the distillation of glycerine there is obtained a dark hygroscopic glycerine-pitch which can be mixed with litharge or red lead to produce a cement. Glycerine is used in this manner to make a cement for optical instruments which is resistant to the action of water; the glycerine pitch-cement resists the action of oils but not the action of water.

II. Qualitative Examination

Glycerol (and consequently glycerides) can be detected by the acrolein test; by heating with potassium bisulphate, water is split out from glycerol, and acrolein with characteristic odor is formed.

$$CH_2OH \cdot CHOH \cdot CH_2OH \rightarrow CH_2 : CH \cdot CHO + 2\,H_2O.$$

If only a very little fat is present, the sample is saponified in the usual manner, the fatty acid separated with mineral acid, the acid filtered and the filtrate evaporated after neutralization with soda. The residue is then tested for glycerine by the bisulphate method.

By another method* the sample to be tested for glycerine is boiled with alcoholic potash, acidified, filtered, the filtrate made alkaline, copper sulphate added, and the solution boiled one minute. If the filtrate from this is blue, glycerine is present.

Small amounts of glycerine (as little as 3 milligrams) may be detected† by oxidation with sodium hypochlorite, and digestion of the glycerose obtained with HCl and orcin; a violet or greenish blue color is produced.

* Wagenaar, Chem. Zentralbl., **1911,** I, 1765; II, 103.

† Mandel and Neuberg, Biochem. Z., **71,** 214 (1915).

III. Quantitative Determination

This determination is of importance in estimating the value of the products of the candle or the soap industries; it is used in fat analysis, only when, for example, it is necessary to test for fats in waxes and substances which are not glycerides. Since the glycerides yield about 10 per cent of glycerine (the glyceryl radical is about 5 per cent of the fat) the amount of neutral fat may be approximately determined from the glycerine content.

(*a*) **Crude Glycerine.** The following methods for the analysis of crude glycerines were recommended by the International Committee on Glycerine Analysis which met in London in October, 1910.*

SAMPLING CRUDE GLYCERINE

The usual method of sampling crude glycerine hitherto has been by means of a glass tube, which is slowly lowered into the drum with the object of taking as nearly as possible a vertical section of the glycerine contained in the drum. This method has been found unsatisfactory, owing to the fact that in cold climates glycerine runs into the tube very slowly, so that, owing to the time occupied, it is impossible to take a complete section of the crude. Another objection to the glass tube is that it fails to take anything approaching a correct proportion of any settled salt contained in the drum.

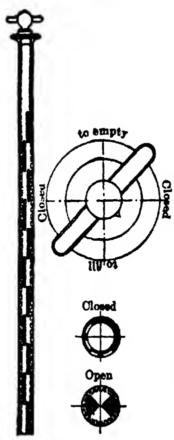


Fig. 130.

The sampler which is illustrated herewith has been devised with the object of overcoming the objections to the glass tube as far as possible. It consists of two brass rods, one fitting closely inside the other. A number of ports are cut out in each tube in such a way that when the ports are opened a continuous slot is formed which enables a complete section to be taken throughout the entire length of the drum. By this arrangement the glycerine fills into the sampler almost instantaneously. There are a number of ports cut at the bottom of the sampler which render it possible to take a proportion of the salt at the bottom of the drum. The instrument is so constructed that all the ports, including the bottom ones, can be closed simultaneously by the simple action of turning the handle at the top; a pointer is arranged which indicates on a dial when the sampler is open or closed. In samplers of larger section (1 inch) it is possible to arrange a third motion whereby the bottom ports only are open for emptying but in samplers of smaller dimensions ($\frac{5}{8}$ inch) this third motion must be dispensed with, otherwise the dimensions of the ports have to be so small that the sampler would not be efficient.

In using the sampler it is introduced into the drum with the ports closed, and when it has touched the bottom, the ports are opened for a second or two, then closed

* Jour. Ind. and Eng. Chem., **3**, 682 (1911); Zeit. f. angew. Chem., **24**, 865 (1911).

and withdrawn, and the sample discharged into the receiving vessel by opening the ports. When the drum contains salt which has deposited, the ports must be opened before the sampler is pushed through the salt, thus enabling a portion to be included in the sample. It is, however, almost impossible to obtain a correct proportion of salt after it has settled in the drum and it is therefore recommended that the drum be sampled before any salt has deposited. A sampler 1 inch in diameter withdraws approximately 10 ounces from a 110-gallon drum. A sampler $\frac{5}{8}$ inches in diameter will withdraw about 5 ounces.

1. **Determination of Free Caustic Alkali.** Put 20 grams of the sample into a 100 c.c. flask, dilute with approximately 50 c.c. of freshly boiled distilled water, add an excess of neutral barium chloride solution, 1 c.c. of phenolphthalein solution, make up to the mark and mix. Allow the precipitate to settle, draw off 50 c.c. of the clear liquid and titrate with normal acid (N/1). Calculate the percentage of sodium oxide existing as caustic alkali.

2. **Determination of Ash and Total Alkalinity.** Weigh 2 to 5 grams of the sample in a platinum dish, burn off the glycerine over a luminous Argand burner or other source of heat,* giving a low temperature, to avoid volatilization and the formation of sulphides. When the mass is charred to the point that water will not be colored by soluble organic matter, lixiviate with hot distilled water, filter, wash and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate the water, and carefully ignite without fusion. Weight the ash.

Dissolve the ash in distilled water and titrate total alkalinity, using as indicator methyl orange cold or litmus boiling.

3. **Determination of Alkali Present as Carbonate.** Take 10 grams of the sample, dilute with 50 c.c. distilled water, add sufficient N/1 acid to neutralize the total alkali found at (2), boil under a reflux condenser for 15 to 20 minutes, wash down the condenser tube with distilled water, free from carbon dioxide, and then titrate back with N/1 sodium hydroxide, using phenolphthalein as indicator. Calculate the percentage of sodium oxide. Deduct the sodium oxide found in (1). The difference is the percentage of sodium oxide existing as carbonate.

4. **Alkali Combined with Organic Acids.** The sum of the percentages of sodium oxide found at (1) and (3) deducted from the percentage found at (2) is a measure of the sodium oxide or other alkali combined with organic acids.

5. **Determination of Acidity.** Take 10 grams of the sample, dilute with 50 c.c. distilled water free from carbon dioxide, and titrate with N/1 sodium hydroxide and phenolphthalein. Express in terms of sodium oxide required to neutralize 100 grams.

6. **Determination of Total Residue at 160° C.** For this determination the crude glycerine should be slightly alkaline with sodium carbonate not exceeding 0.2 per cent sodium oxide, in order to prevent loss of organic acids. To avoid the formation of polyglycerols this alkalinity must not be exceeded.

Ten grams of the sample are put into a 100 c.c. flask, diluted with water and the calculated quantity of N/1 hydrochloric acid or sodium carbonate added to give the required degree of alkalinity. The flask is filled to 100 c.c., the contents mixed, and 10 c.c. measured into a weighed Petrie or similar dish 2.5 inches in diameter and 0.5 inch deep, which should have a flat bottom. In the case of crude glycerines

* Carbon is readily burned off completely, without loss of chlorides, in a gas-heated muffle furnace adjusted to a dull red heat.

abnormally high in organic residue a smaller amount should be taken, so that the weight of the organic residue does not materially exceed 30 to 40 milligrams.

The dish is placed on a water bath (the top of the 160° oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven* measuring 12 inches cube, having an iron plate 0.75 inch thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf halfway up the oven. On these strips the dish containing the glycerine is placed.

If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130° to 140° can be readily maintained with the door partially open, and the glycerine, or most of it, should be evaporated off at this temperature. When only a slight vapor is seen to come off, the dish is removed and allowed to cool.

An addition of 0.5 to 1.0 c.c. of water is made, and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spurt. The time taken up to this point cannot be given definitely, nor is it important. Usually two or three hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained, at 160° C. for an hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, etc., is repeated until a constant loss of 1 to 1.5 mg. per hour is obtained.

In the case of acid glycerine a correction must be made for the alkali added; 1 c.c. N/1 alkali represents an addition of 0.03 gram. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the sodium hydroxide and sodium carbonate to sodium chloride. The corrected weight multiplied by 100 gives the percentage of total residue at 160° C.

This residue is taken for the determination of the non-volatile acetylizable impurities (see acetin method).

7. **Organic Residue.** Subtract the ash from the total residue at 160° C. Report as organic residue at 160° C. (it should be noted that alkaline salts of fatty acids are converted to carbonates on ignition and that the carbon dioxide thus derived is not included in the organic residue).

8. **Moisture.** Glycerine can be completely freed from moisture by standing in a vacuum over concentrated sulphuric acid or phosphoric anhydride.

2 to 3 grams of voluminous asbestos (previously washed with acids and then dried in a steam drying closet) are placed in a weighed bottle of 15 c.c. capacity. The bottle is then kept in a vacuum desiccator (at 1 to 2 mm. mercury pressure), over sulphuric acid till the weight is constant; then 1 to 1.5 grams of the sample are dropped carefully on the asbestos so that the glycerine is completely absorbed. The bottle with contents is then weighed and kept in a desiccator (at 1 to 2 mm.

* An electric oven suitable for this work, which is readily adjusted to 160° C., has been made for A. C. Langmuir and W. H. Low, by the Apparatus and Specialty Co., Lansing, Mich. Its size is 9½ × 10 × 16 inches and capacity 8 Petrie dishes. It gives a strong draft at constant temperature.

pressure) till the weight has become constant; this will require about 48 hours at 15° (longer at lower temperatures). The sulphuric acid in the desiccator must be frequently renewed.

ACETIN PROCESS FOR THE DETERMINATION OF GLYCEROL

This process is the one agreed upon at a conference of delegates from the British, French, German and American committees, and has been confirmed by each of the above committees as giving results nearer to the truth than the bichromate method on crudes in general. It is the process to be used (if applicable) whenever only one method is employed. On pure glycerines the results are identical with those obtained by the bichromate process. For the application of this method the crude glycerine should not contain over 50 per cent water. The errors of the method have been discussed.*

REAGENTS REQUIRED

(*A*) **Best Acetic Anhydride.** This should be carefully selected. A good sample must not require more than 0.1 normal sodium hydroxide for saponification of the impurities when a blank is run on 7.5 c.c. Only a slight color should develop during digestion of the blank.

The anhydride may be tested for strength by the following method: Into a weighed stoppered vessel, containing 10 to 20 c.c. of water, run about 2 c.c. of the anhydride, replace the stopper and weigh. Let stand with occasional shaking, for several hours, to permit the hydrolysis of all the anhydride; then dilute to about 200 c.c., add phenolphthalein and titrate with N/1 sodium hydroxide. This gives the total acidity due to free acetic acid and acid formed from the anhydride. It is worthy of note that in the presence of much free anhydride a compound is formed with phenolphthalein, soluble in alkali and acetic acid, but insoluble in neutral solutions. If a turbidity is noticed toward the end of the neutralization it is an indication that the anhydride is incompletely hydrolyzed and inasmuch as the indicator is withdrawn from the solution, results may be incorrect.

Into a stoppered weighing bottle containing a known weight of recently distilled aniline (from 10 to 20 c.c.) measure about 2 c.c. of the sample, stopper, mix, cool and weigh. Wash the contents into about 200 c.c. of cold water, and titrate the acidity as before. This yields the acidity due to the original, preformed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated to 100 grams) and double the result, obtaining the c.c. N/1 sodium hydroxide per 100 grams of the sample. 1 c.c. N/1 sodium hydroxide equals 0.0510 anhydride.

(*B*) **Pure Fused Sodium Acetate.** The purchased salt is again completely fused in a platinum, silica or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or desiccator. It is most important that the sodium acetate be anhydrous.

(*C*) **A Solution of Caustic Soda for Neutralizing, of about N/1 Strength, Free from Carbonate.** This can be readily made by dissolving pure sodium hydroxide

* Tortelli, Chem. Ztg., **37**, 1505, 1573 (1913); **38**, 3, 28, 46 (1914).

in its own weight of water (preferably water free from carbon dioxide) and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

(*D*) **N/1 Caustic Soda Free from Carbonate.** Prepared as above and carefully standardized. Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

(*E*) **N/1 Acid.** Carefully standardized.

(*F*) **Phenolphthalein Solution.** 0.5 per cent phenolphthalein in alcohol and neutralized.

THE METHOD

In a narrow-mouthed flask (preferably round-bottomed), capacity about 120 c.c., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25 to 1.5 grams of the glycerine. A Grethan or Lunge pipette will be found convenient. Add about 3 grams of the anhydrous sodium acetate; then 7.5 c.c. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside diameter. The flask is connected to the condenser by either a ground glass joint (preferably) or by a rubber stopper. If a rubber stopper is used it should have had a preliminary treatment with hot acetic anhydride vapor.

Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat, and through the condenser tube add 50 c.c. of distilled water free from carbon dioxide at a temperature of about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapors from the flask on adding water and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment, bearing in mind that the anhydride in excess is much more effectively hydrolyzed in hot than in cold water. The contents of the flask may be warmed to, but must not exceed, 80° C., until the solution is complete, except a few dark flocks representing organic impurities in the crude. By giving the flask a rotary motion, solution is more quickly effected.

Cool the flask and contents without loosening from the condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off the stopper or ground glass connection into the flask, and filter the contents through an acid-washed filter into a Jena glass flask of about 1 liter capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 c.c. of phenolphthalein solution (*F*), then run in caustic soda solution (*C*) or (*D*) until a faint pinkish yellow color appears throughout the solution. This neutralization must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralized, as indicated by the slower disappearance of the color developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 c.c. or a calculated excess of N/1 NaOH (*D*)

and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate the excess of NaOH with N/1 acid (*E*) until the pinkish yellow or chosen end-point color just remains.* A further addition of the indicator at this point will cause an increase of the pink color; this must be neglected, and the first end-point taken.

From the N/1 NaOH consumed calculate the percentage of glycerol (including acetylizable impurities) after making the correction for the blank test described below.

1 c.c. N/1 NaOH = 0.03069 gram glycerol.

The coefficient of expansion for normal solutions is 0.00033 per c.c. for each degree centigrade. A correction should be made on this account if necessary.

Blank Test. As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride, sodium acetate and water as in the analysis. It is not necessary to filter the solution of the melt in this case, but sufficient time must be allowed for the hydrolysis of the anhydride before proceeding with the neutralization. After neutralization it is not necessary to add more than 10 c.c. of the N/1 alkali (*D*), as this represents the excess usually present after the saponification of the average soap lye crude. In determining the acid equivalent of the N/1 NaOH, however, the entire amount taken in the analysis, 50 c.c., should be titrated after dilution with 300 c.c. water free from carbon dioxide and without boiling.

Determination of the Glycerol Value of the Acetylizable Impurities. The total residue at 160° C. is dissolved in 1 or 2 c.c. of water, washed into the acetylizing flask and evaporated to dryness. Then add anhydrous sodium acetate and acetic anhydride in the usual amounts and proceed as described in the regular analysis. After correcting for the blank, calculate the result to glycerol.

Instructions for Calculating the Actual Glycerol Content.

(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylizable impurities if any are present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylizable impurities are present these are included in this figure.

BICHROMATE PROCESS FOR GLYCEROL DETERMINATION

Reagents Required

(*A*) **Pure Potassium Bichromate** powdered and dried in air free from dust or organic vapors, at 110° to 120° C. This is taken as the standard.

(*B*) **Dilute Bichromate Solution.** 7.4564 grams of the above bichromate are dissolved in distilled water and the solution made up to one liter at 15.5° C.

(*C*) **Ferrous Ammonium Sulphate.** It is never safe to assume this salt to be constant in composition and it must be standardized against the bichromate as

* A precipitate at this point is an indication of the presence of iron or alumina, and high results will be obtained unless a correction is made as described below.

follows: dissolve 3.7282 grams of bichromate (A) in 50 c.c. of water. Add 50 c.c. of 50 per cent sulphuric acid (by volume), and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute bichromate (B). Calculate the value of the ferrous salt in terms of bichromate.

(D) **Silver Carbonate.** This is prepared as required for each test from 104 c.c. of 0.5 per cent silver sulphate solution by precipitation with about 4.9 c.c. N/1 sodium carbonate solution (a little less than the calculated quantity of N/1 sodium carbonate should be used as an excess prevents rapid settling). Settle, decant and wash once by decantation.

(E) **Subacetate of Lead.** Boil a 10 per cent solution of pure lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(F) **Potassium Ferricyanide.** A very dilute, freshly prepared solution containing about 0.1 per cent.

THE METHOD

Weigh 20 grams of the glycerine, dilute to 250 c.c. and take 25 c.c. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and add a slight excess (about 5 c.c. in most cases) of the basic lead acetate (E), allow to stand a few minutes, dilute with distilled water to 100 c.c., and then add 0.15 c.c. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 c.c., and return the filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate (in the great majority of cases 5 c.c. are ample, but occasionally a crude will be found requiring more, and in this case another aliquot of 25 c.c. of the dilute glycerine should be taken and purified with 6 c.c. of the basic acetate). Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 c.c. of the clear filtrate into a flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3.7282 grams of the powdered potassium bichromate (A). Rinse down the bichromate with 25 c.c. of water and let stand with occasional shaking until all the bichromate is dissolved (no reduction will take place in the cold).

Now add 50 c.c. of 50 per cent sulphuric acid (by volume) and immerse the vessel in boiling water for two hours and keep protected from dust and organic vapors, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (C), making spot tests on a porcelain plate with the potassium ferricyanide (F). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 gram glycerol = 7.4564 grams bichromate.

1 gram bichromate = 0.13411 gram glycerol.

The percentage of glycerol obtained above includes any oxidizable impurities present after the purification. A correction for the non-volatile impurities may be made by running a bichromate test on the residue at 160° C.

NOTES

(1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(2) Before the bichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with sulphuric acid, as stipulated.

(3) For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0.5 c.c.

(4) It is sometimes advisable to add a little potassium sulphate to insure a clear filtrate.

REMARKS

It has been shown by experience that in good crude glycerine, the sum of water, total residue at 160° and corrected glycerine content will be equal to 100 ± 0.5 per cent. Moreover with such samples, the bichromate method will agree with the acetin result to within 1 per cent.

If larger differences are found, then impurities, such as polyglycerines or trimethylene glycol, are present. Trimethylene glycol is more volatile than glycerine; it can therefore be isolated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and bichromate results on such distillates. Trimethylene glycol shows by the first method 80.69 per cent and by the second 138.3 per cent glycerine. In valuing the crude glycerine for some purposes, the determination of its approximate content of arsenic, sulphides, sulphites and thiosulphates is necessary. The methods for the determination of these components were not included in the report.

If the non-volatile, organic residue at 160° be more than 2.5 per cent of glycerine (without correcting for the carbon dioxide in the ash), the residue is to be tested by the acetin method, and the glycerine content found, which exceeds 0.5 per cent, is to be subtracted from the acetin result. With saponification glycerine and similar glycerines, the organic residue is to be neglected if it does not exceed 1 per cent. If the sample should contain more than 1 per cent, the organic residue must be acetylated and the glycerine found (after subtracting 0.5 per cent) subtracted from the acetin value.

Hehner-Steinfels Modification* of the Bichromate Method. This modification of the bichromate method has been found useful and has found application in the examination of hardened oils.

Ten grams of glycerine liquor or 2 grams of crude glycerine are washed into a 200 c.c. graduated flask, 20 c.c. of ten per cent zinc sulphate solution are added, and then water added to the mark; the resulting precipitate is allowed to settle. A portion of the supernatant liquid is run through a dry filter into a dry flask (turbidity need not cause concern); 20 c.c. of the filtrate are pipetted into a 250 c.c. flask, 25 c.c. of Hehner solution (74.564 gram of very pure $K_2Cr_2O_7$ + 150 c.c. of concentrated H_2SO_4, diluted to one liter) are added and finally the walls of the flask washed with 50 c.c. of sulphuric acid (250 gram H_2SO_4 + 750 grams of water). A beaker

* Seifenfabrikant, **25,** 1265 (1905); **30,** 505 (1910). Seifensiederztg., **41,** 1257 (1914). Also Davidsohn, Seifensiederztg., **41,** 1194, 1301 (1914). Normann and Hugel, Chem. Umschau, **23,** 45 (1916).

is inverted over the flask which is heated 2 hours on a boiling water-bath. The somewhat cooled liquid is brought quantitatively into a 500 c.c. graduated flask, water is added to the mark, and the mixture then shaken.

To determine the amount of bichromate not used for oxidation 50 c.c. of the solution in the graduated flask is added to 2 grams of KI and 25 c.c. of 20 per cent HCl, water is added to make 500 c.c., and the solution then titrated with N/10 thiosulphate in the presence of starch

A blank test is run with 25 c.c. of the Hehner bichromate solution with 50 c.c. of sulphuric acid (250 gram in 1 liter), with water added to make 500 c.c. exactly; of this mixture 50 c.c. are titrated with $\frac{N}{10}$ thiosulphate (in the presence of potassium iodide).

One cubic centimeter of $\frac{N}{10}$ thiosulphate is equivalent to 0.00065757 gram of glycerine. If the bichromate solution is made up exactly as indicated, the blank test will be unnecessary. If the temperature differs considerably from 15° C. the following corrections should be made: —

Temperature of bichromate solution	Value of thiosulphate at 15°	Temperature of bichromate solution	Value of thiosulphate at 15°
°C.	c.c.	°C.	c.c.
11	50.10	18	49.93
12	50.07	19	49.90
13	50.05	20	49.87
14	50.02	21	49.85
15	50.00	22	49.82
16	49.98	23	49.80
17	49.95		

(*b*) **Pure Glycerol.** Besides the methods given in (*a*) the following are also in use:

1. The method of Benedikt and Zsigmondi depends on the oxidation of glycerine to oxalic acid by the action of permanganate in alkaline solution according to the equation:

$$C_3H_5(OH)_3+4\ KMnO_4+4\ KOH \rightarrow C_2H_2O_4+4\ K_2MnO_3+CO_2+5\ H_2O$$
$$C_3H_5(OH)_3 + 3\ O_2 \rightarrow C_2H_2O_4 + CO_2 + 3\ H_2O.$$

2 to 3 grams of fat are saponified with KOH and methyl alcohol; the fatty acids are separated from the soap (page 406) and well washed. The combined filtrate is clarified by filtration through a double filter-paper, then washed, neutralized with potassium hydroxide and diluted with a solution of 10 grams of KOH in 300 c.c. of water. To this solution 5 per cent permanganate is added till the liquid is colored blue or black. After standing ½ hour, hydrogen peroxide is added, not in great excess, to decompose the unchanged permanganate. The colorless solution is put into a liter graduated flask and water added up to the mark; 500 c.c. are then filtered, heated to boiling for ½ hour to decompose the excess hydrogen peroxide,

cooled to 60° and the oxalic acid titrated with N/10 permanganate. Two molecular weights of permanganate are equivalent to five molecular weights of glycerol, the oxidation in acid solution taking place according to the equation:

$$5\,C_2H_2O_4 + 2\,KMnO_4 + 3\,H_2SO_4 \rightarrow 8\,H_2O + 10\,CO_2 + K_2SO_4 + 2\,MnSO_4.$$

This method gives exact results only when no other oxidizable substances are present.*

2. The method of Shukoff and Schestakoff† has also been found useful industrially,‡ the agreement of the results by the extraction and the acetin methods being very good, although in some cases the values obtained by the extraction method are somewhat high.

The glycerol is directly determined by evaporating the glycerine solution (below 80°) to a syrup which is then mixed with anhydrous sodium sulphate and this mixture extracted with acetone in a Soxhlet apparatus. By evaporation of the solvent under 80° the residual glycerol can be weighed.

3. In the method of Zeisel and Fanto§ hydriodic acid is allowed to act on glycerine with the formation of isopropyl iodide which after volatilization is allowed to react with silver nitrate with the formation of silver iodide and propylene.

$$C_3H_5(OH)_3 + 5\,HI \rightarrow C_3H_7I + 3\,H_2O + 2\,I_2.$$

$$C_3H_7I + AgNO_3 \rightarrow AgI + C_3H_6 + HNO_3.$$

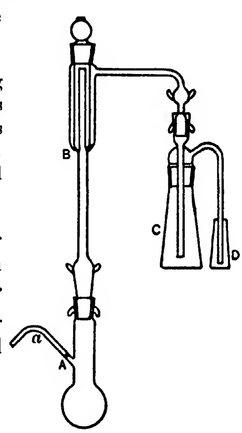


FIG. 131.

Twenty grams of fat are saponified with alcoholic alkali and after evaporation of the alcohol, acidified with acetic acid, and the fatty acids separated in the customary manner. A part of the glycerine solution (not more than 5 c.c., since otherwise the hydriodic acid will be too much diluted) is put into the flask A of the apparatus (Fig. 131), together with some pumice stone and 15 c.c. of hydriodic acid (sp. gr. 1.9); in the examination of dry substances (in which case only enough should be taken to give 0.4 gram of AgI) a 58 per cent acid of specific gravity 1.7 may be used. The apparatus is immediately connected and a stream of carbon dioxide run through the tube a at the rate of 3 bubbles per second; the flask is gently heated by means of a glycerine bath, the distillate passing through B which contains 5 c.c. of water and 0.5 gram of red phosphorus to remove hydriodic acid and iodine from the distillate. The phosphorus should have been previously washed free from impurities by treatment with carbon bisulphide, ether, alcohol and water. The purified isopropyl iodide passes into the wash bottle containing 45 c.c. of the silver

* Willstätter, Ber., **45**, 2825 (1912).

† Zeit. f. angew. Chem., **18**, 294 (1905).

‡ Landsberger, Chem. Rev., **12**, 150 (1905).

§ Zeit. f. d. Landwirt. Versuchswesen in Oesterreich, **5**, 729 (1902).

nitrate and here the silver iodide separates; a safety flask with 5 c.c. of silver nitrate solution is attached (D). The silver nitrate solution is prepared by dissolving 40 grams of fused silver nitrate in 100 c.c. of water and then diluting to 1 liter with absolute alcohol; it should be filtered after 24 hours and also before use. The distillation lasts 2 to 4 hours; the end point is determined by changing the silver nitrate solution. To determine the amount of silver iodide formed, the material is washed into a beaker, diluted to 450 c.c., 10 to 15 drops of nitric acid added and the analysis then carried on in the usual manner. The amount of silver iodide multiplied by 0.3922 gives the weight of glycerol present

Sulphur compounds, alcohols, esters and ethers, in so far as they form volatile iodides, interfere with the determination and must therefore be removed by distillation or by extraction with the proper solvents; sulphates are prevented from interfering by treatment with barium acetate.

Lewkowitsch*considered the method inexact, but F. Schulze† was able to get very accurate results with it; in Austria it has been much used commercially.

The disadvantages of the method (use of large amounts of fat and hydriodic acid, use of alcoholic alkali and therefore the errors caused by alcohol) are overcome by the following modification of Willstätter and Madinaveitia:‡

About 0.2 gram of the glyceride is weighed into the generating flask and 10 c.c. of hydriodic acid of 1.8 specific gravity added; by warming the bath up to 115° the reaction begins as is shown by the precipitation of silver iodide in the wash bottle. The temperature is kept constant for 40 minutes, or till the solution has cleared; the temperature is then raised to 135° and kept at that point for an hour.

This method avoids the use of large amounts of fat and saponification is unnecessary; the results as obtained are somewhat lower than those obtained by the Zeisel-Fanto method.

Physical Constants of Pure Glycerol

Specific gravity at 15°	1.2653
Coefficient of expansion	0.00062
Index of refraction at 20°	1.4729
Boiling point at 760 mm. pressure	290°
Boiling point at 50 mm. pressure	210°
Boiling point at 12.5 mm. pressure	179.5°
Boiling point at 10 mm. pressure	162°
Boiling point at 0.25 mm. pressure	143°

* Analysis, I, 311.
† Chem. Ztg., **29**, 976 (1905).
‡ Ber., **45**, 2825 (1912).

TABLE 106

SPECIFIC GRAVITY AND INDEX OF REFRACTION OF GLYCERINE IN AQUEOUS SOLUTION*

Anhydrous glycerine, %	Specific gravity (12–14° C.)	Refractive index (12.5–12.8° C.)	Anhydrous glycerine, %	Specific gravity (12–14° C.)	Refractive index (12.5–12.8° C.)	Anhydrous glycerine, %	Specific gravity (12–14° C.)	Refractive index (12.5–12.8° C.)	Anhydrous glycerine, %	Specific gravity (12–14° C.)	Refractive index (12.5–12.8° C.)
100	1.2691	1.4758	74	1.1999	1.4380	49	1.1293	1.3993	24	1.0608	1.3639
99	1.2664	1.4744	73	1.1973	1.4366	48	1.1265	1.3979	23	1.0580	1.3626
98	1.2637	1.4729	72	1.1945	1.4352	47	1.1238	1.3964	22	1.0553	1.3612
97	1.2610	1.4715	71	1.1918	1.4337	46	1.1210	1.3950	21	1.0525	1.3599
96	1.2584	1.4700	70	1.1889	1.4321	45	1.1183	1.3935	20	1.0498	1.3585
95	1.2557	1.4686	69	1.1858	1.4304	44	1.1155	1.3921	19	1.0471	1.3572
94	1.2531	1.4671	68	1.1826	1.4286	43	1.1127	1.3906	18	1.0446	1.3559
93	1.2504	1.4657	67	1.1795	1.4267	42	1.1100	1.3890	17	1.0422	1.3546
92	1.2478	1.4642	66	1.1764	1.4249	41	1.1072	1.3875	16	1.0398	1.3533
91	1.2451	1.4628	65	1.1733	1.4231	40	1.1045	1.3860	15	1.0374	1.3520
90	1.2425	1.4613	64	1.1702	1.4213	39	1.1017	1.3844	14	1.0349	1.3507
89	1.2398	1.4598	63	1.1671	1.4195	38	1.0989	1.3829	13	1.0332	1.3494
88	1.2372	1.4584	62	1.1640	1.4176	37	1.0962	1.3813	12	1.0297	1.3480
87	1.2345	1.4569	61	1.1610	1.4158	36	1.0934	1.3799	11	1.0271	1.3467
86	1.2318	1.4555	60	1.1582	1.4140	35	1.0907	1.3785	10	1.0245	1.3454
85	1.2292	1.4540	59	1.1556	1.4126	34	1.0880	1.3772	9	1.0221	1.3442
84	1.2265	1.4525	58	1.1530	1.4114	33	1.0852	1.3758	8	1.0196	1.3430
83	1.2238	1.4511	57	1.1505	1.4102	32	1.0825	1.3745	7	1.0172	1.3417
82	1.2212	1.4496	56	1.1480	1.4091	31	1.0798	1.3732	6	1.0147	1.3405
81	1.2185	1.4482	55	1.1455	1.4079	30	1.0771	1.3719	5	1.0123	1.3392
80	1.2159	1.4467	54	1.1430	1.4065	29	1.0744	1.3706	4	1.0098	1.3380
79	1.2122	1.4453	53	1.1403	1.4051	28	1.0716	1.3692	3	1.0074	1.3367
78	1.2106	1.4438	52	1.1375	1.4036	27	1.0689	1.3679	2	1.0049	1.3355
77	1.2079	1.4424	51	1.1348	1.4022	26	1.0663	1.3666	1	1.0025	1.3342
76	1.2046	1.4409	50	1.1320	1.4007	25	1.0635	1.3652	0	1.0000	1.3330
75	1.2016	1.4395		.	..	.	....	...	..	..	....

* Lunge-Berl., Bd. III, 763.

Specification for Glycerine for Artillery Purposes

Imperial Wharves, Wilhelmshaven

The glycerine must be clear, colorless and odorless, sweet, neutral and without free acid, and should have a specific gravity of 1.151 to 1.157 at 15°. If 1 c.c. of glycerine is mixed with 3 c.c. of stannous chloride solution, the mixture must not assume a dark color in the course of an hour. Diluted with 5 parts of water the glycerine must not react with hydrogen sulphide, ammonium oxalate, barium nitrate or calcium chloride; only a faint cloudiness should be given with silver nitrate. Five c.c. heated to boiling in an open dish and ignited should leave only a dark residue which completely disappears on stronger heating. A mixture of 1 gram glycerine and 1 c.c. of an ammonia solution heated to 60° in a water bath and then treated with 3 drops of silver nitrate solution should after 5 minutes show neither a coloration nor a brown precipitate. One c.c. of glycerine warmed with 1 c.c. of sodium hydroxide should not become colored or develop an odor of ammonia or

of glue; 1 c.c. gently warmed with 1 c.c. of sulphuric acid should not develop an unpleasant odor.

For dynamite glycerine the following test is described by Heller:*

Twenty-five grams of glycerine are run drop by drop into a beaker (12 cm. high, 8 cm. wide) containing 150 grams of mixed acids (1 part by weight of fuming nitric, specific gravity 1.5 and 2 parts of concentrated sulphuric acid, specific gravity 1.845); the temperature should not rise above 30° and should preferably be kept under 20°. After nitration, the mixture is transferred to a dry, narrow graduated cylinder and carefully observed to see if the separation of the layers takes place rapidly or at most within 10 minutes and if the surface of separation is bright or not.

D. Soaps

I. General

Soaps, that is, alkali salts of the higher fatty acids, are obtained by a boiling, or by a cold saponification, of fats with strong lyes, or of fatty acids with sodium or potassium carbonates. For some time the making of soaps from the fatty acids has been preferred by many manufacturers, because the preceding hydrolysis of fats in autoclaves, or by the Twitchell method, or by enzymes is made more profitable by the simultaneous preparation of a relatively pure glycerine.

After the fats have been saponified in large kettles, the hot viscous soaps are cooled, cut in slabs and shaped in bars under pressure. For toilet soaps the soap is dried in thin slices, mixed with perfume, coloring materials and substances of medicinal value, and then rolled into slabs from which the usual bars are obtained.

All animal and vegetable oils and fats may be considered as raw materials for the manufacture of soap, though usually the cheaper materials are used except for the production of toilet or medicinal soaps; hardened oils are also used. The fats with low iodine values are used for producing the ordinary hard soaps; soft soaps are made from fats with higher iodine values.

Soft soaps are potassium soaps; they contain all the glycerine which has been formed, if the soaps are made from the fats themselves and not from fatty acids, and also excess lye or fat, salts and all impurities in the original material. The much desired granular appearance of the soft soaps is due to the crystallization of potassium stearate and palmitate. Recently, solid potassium soaps have been prepared by using high-melting fats and waxes (Japan wax, spermaceti, Chinese wax and beeswax).

* Einheitsmethoden, 85.

Hard soaps are made either by the cold process of stirring the fat (cocoanut oil and palm nut oil) with strong soda lye, or by boiling the fat with soda lye, or the fatty acids with soda; in the Krebitz process of making soap, the fats are changed into calcium soaps with lime and these, after filtration and leaching with water to extract glycerine, are decomposed with sodium carbonate. This latter process is said to yield a better glycerine. The hard soaps are generally salted out by the addition of sodium chloride and thus separated from the glycerine solution underneath; cold process soaps, as well as filled soaps, which are generally obtained from cocoanut oil, are not salted out and consequently they contain more water than the curd soaps (as the salted-out product is known) in which the water may range from 10 to 30 per cent. The cold process soaps also contain glycerine, excess alkali and impurities, and often filling material.

Toilet soap (especially lanolin soap) may contain a slight amount of free alkali (0.06 to 0.08 per cent); this may react slowly with fatty acid or fat present in the soap. Lanolin soaps may contain 8 to 10 per cent of purified wool fat, added after the actual saponification process. Such additions are not made to laundry soaps, though in toilet soaps they have a beneficial action on the skin.

Soaps which float on water are produced by stirring air into the semi-solid soap, the product having a density less than that of water. Transparent soaps are produced by action of alcohol or sugar; crystallization being prevented, the soaps remain transparent. Medicated soaps are milled soaps to which have been added the particular pharmaceutical material; the material added must not react with the soap.

II. Colloidal Nature and Hydrolysis of Aqueous Soap Solutions*

According to the modern viewpoint soap is a colloid. Aqueous solutions when treated with electrolytes allow the separation of a soap gel; such gels show the typical behavior of a solid colloid, the ability to adsorb part of the precipitating electrolyte. The soaps of acids of higher molecular weight are salted out more easily than soap of lower-molecular-weight acids, that is, with less electrolyte; soaps of unsaturaated acids require more salt for salting out. Soap made from cocoanut oil (containing much lauric acid) is not easily precipitated; the soap from tallow (rich in stearic acid) precipitates easily. The concentra-

* Merklen, Die Kernseifen, Halle 1907. Richert, Aussalzen von Seifen, Inauguraldissertation, Karlsruhe, 1911.

tion of the electrolytes which prevents resolution of the soap is also a function of the kind of ions. Sodium salts have a greater precipitating action than potassium salts; the hydroxides are most active, the chlorides less so, carbonates least active.

TABLE 107

EQUIVALENT CONDUCTANCE OF ALKALI SALTS OF FATTY ACIDS

Potassium

Mols in 1000 grams of water	1 0	0 75	0 5	0 2	0 1	0 05	0 02	0 01
Stearate	113 4	112 6	113.9	100 0	96 0	101 7	124 9	147.7
Palmitate	124 2	127 9	127 0	111 0	107 0	110 8	133 2	171 6
Myristate	136 2	.	135.4	130 8	121 8	136 6	181.6	242.3
Laurate	143.3	142 6	146.0	144.2	159 7	195.6		233.0
Caprate	145.9	.	156 3	180 9	200.6	211.9		232 4
Caprylate	148.7	. . .	168.5	191 0	205.2	219 2	.	239 5
Capronate	149.5	.	177.7	201 2	216 5	227 7		245.9
Acetate	176 9	183.9	196.6	221.2	236 5	249 5	262.6	270.4

Sodium

Mols in 1000 grams of water	1 5	1 0	0.75	0 50	0 35	0 20	0 10	0 05	0 01
Stearate	81 5	88 3	.	76 1	.	77.4	76 0	78 0	125 9
Palmitate	84.5	84 7	87 5	89.5	87.0	82.4	82.5	88.6	137 7
Myristate	84.8	94.9	97.6	99.2	.	95 2	96.5	110.4	191.7
Laurate	96.2	104 2		109.5	. . .	113.4	125.5	152.0	193.9
Caprylate	....	..	...	. .	....	. .	.	..	...
Capronate	....	. .	. .	..	...				. . .
Acetate	....	129.7	138.6	154.0	...	178.9	195.0	207.8	228.2

The salted-out soap contains water, electrolyte and glycerine; the amount of adsorbed material depends on the concentration of the solution; from a concentrated salt solution, more salt and less water is adsorbed than from a more dilute solution. Electrolytes also affect* the viscosity and conductance. Potassium salts of lauric, oleic and myristic acids have been studied. A small addition of potassium hydroxide lowers the viscosity of the soaps, but larger amounts may bring about gelatinization. A mixture of KOH and soap has a conductivity

* Goldschmidt and Weissmann, Z. Chem. u. Ind. D Kolloide, **12**, 18 (1913). Kurzmann, Kolliod Chemische Beihefte, S, 427 (1914).

less than the calculated; in higher concentrations of KOH it may be actually less than that of hydroxide alone. McBain* and co-workers have shown that the conductivities of sodium and potassium soaps show certain anomolies. From potassium stearate to potassium laurate (as shown in Table 107) well-marked minima of equivalent conductance are shown. Salts of these acids (stearic to lauric) are the valuable components of soap mixtures. Similar effects are recognized with sodium soaps.

The degree of hydrolysis of aqueous soap solutions has been determined by electromotive force measurements. It is small at 90°. In dilute solutions (0.01 molar) only 6 per cent is hydrolyzed. See Table 108.

TABLE 108

DEGREE OF HYDROLYSIS OF ALKALI SOAPS

Mols in 1000 grams of water	Per cent hydrolyzed	Mols in 1000 grams of water	Per cent hydrolyzed
Sodium palmitate		Potassium palmitate	
1.00	0.20	1.00	0.08
0.75	0.20	0 75	0.31
0.50	0 37	0.50	0 63
0 30	0.50	0.20	0.64
0 10	1.28	0 10	1.25
0 05	2 22	0 05	2 02
0 01	6 6	0 02	5 6
.	. .	0 01	6 8

This small degree of hydrolysis contradicts the assumption of Kahlenburg and Schreiner† that the conductance of soap solutions is due to the free alkali. The boiling point of the soap solutions is not higher than would correspond to the alkali ions alone; palmitate ions do not appear to be present as such. McBain assumes the presence of electrically conducting, highly charged aggregates (so-called ion-micellae) which have a mobility of the order of magnitude of ordinary ions. An increase of conductivity on dilution is due to the dissociation of these aggregates into simple palmitate ions. The concentration of hydroxyl ions is not altered by the addition of palmitic acid

* Berichte, **43**, 321 (1910). Z. physikal. Chem., **76**, 179 (1911). J. Chem. Soc., **99**, 191 (1911); **101**, 2042 (1912); **105**, 417 (1914). Kolloid. Ztg., **12**, 256 (1913). Seifenfabrikant, **35**, 255, 279, 301, 323 (1915).

† Z. physikal. Chem., **27**, 552 (1898).

to palmitate solutions; the solution remains alkaline even on the addition of one mol of palmitic acid to one mol of alkali palmitate. The "acid soap" produced is however probably not a true compound; "adsorption" takes place, the ratio of acid to palmitate may vary. Soap and water react to produce an acid soap and free alkali hydroxide. On the addition of free acid an acid soap is produced; by adding free alkali the hydrolysis is almost prevented. On the addition of considerable free alkali, the free alkali does not disappear, which would indicate that a "basic soap" does not form. Dilute sodium chloride lowers the alkalinity of palmitate solutions; more concentrated solutions increase the alkalinity.

The hydrolysis of soap solutions becomes complete when one of the products is removed from the solution;* it was found that from a solution of one gram of sodium palmitate in 400 c.c. of water the entire free acid could be extracted by toluol.

III. Hydrolysis of Alcoholic Soap Solutions

The hydrolysis of aqueous soap solutions is decreased at room temperatures by the addition of alcohol. Forty per cent of ethyl alcohol or fifteen per cent of amyl alcohol are said† to practically prevent hydrolysis.

However, by shaking a neutral soap solution, containing 50 per cent of alcohol, with naphtha or benzol, Holde‡ was able to extract a considerable amount of free acid, the acid being more soluble in the naphtha or benzol than in the alcoholic soap solution. In the presence of 80 per cent alcohol, hydrolysis was almost completely prevented.

When alcoholic soap solutions are shaken with naphtha, ether, or benzol, or when excess alkali is titrated back in a benzol solution of a dark oil, or free acid is determined in consistent fats (greases), it is well to consider the possible hydrolytic decomposition of the soap solutions in order that errors may be prevented. The amount of acid split off hydrolytically in soap solutions increases with the amount of naphtha and the number of extractions.

Schapringer§ seems to have shown that the per cent of hydrolysis increases with the molecular weight of the acid; oleic acid acts as a strong acid, and therefore shows only a slight amount of hydrolysis.

* Krafft and Wiglow, Berichte, **28**, 2566 (1895).

† Berichte, **36**, 403 (1903).

‡ Z. Electrochemie, **12**, 436 (1910).

§ Dissertation, Karlsruhe, 1911.

67 per cent of alcohol was able to prevent the hydrolysis of sodium laurate, 75 per cent was required for sodium myristate, 84 per cent for palmitate and 95 per cent alcohol was necessary for sodium stearate.

Hirsch* finds that a solution of soap in 95 per cent alcohol to which is added phenolphthalein turns red on boiling; this is said† to be due to an alcoholysis of the soap. Goldschmidt‡ assumes that hydrolysis takes place here also. An equilibrium is established as follows:—

$$R \cdot COOK + C_2H_5OH \rightleftarrows R \cdot COOH + C_2H_5OK$$

The alkaline reaction results from a secondary decomposition of the ethylate by the small amount of water:—

$$C_2H_5OK + H_2O \rightleftarrows KOH + C_2H_5OH$$

IV. Detergent and Disinfecting Action of Soap

The assumption that the detergent action of soap is due to the alkali formed by the hydrolysis of the soap seems to be inadequate; McBain has shown that the alkali concentration is so low that a saponifying action on neutral fat is improbable. Moreover Reychler§ has shown that a free acid, cetylsulphonic acid, has a detergent action. The ability of aqueous soap solutions to emulsify fatty and mineral oils is very important in removing them from the textile materials. Reychler considers that the poly-molecular micelli present in soap solutions take up the fatty dirt particles. The soap decreases the surface tension between fat and water, penetrates into the finest capillaries of the fabrics and brings about a wetting and emulsification of grease particles. The most efficient concentration for decreasing the surface tension between water and oil has been found by Donnan and Potts‖ to be $\frac{N}{300}$; this gives the maximum emulsifying power. Plateau¶ and Quincke** state that the surface tension of soap solutions is only 40 per cent of that of pure water; water will rise in a capillary 2.6 times as high as soap solution. By efflux from a stalagmometer, a drop-counting burette, soap solutions form 2.6 times as many drops as water does. The lathering of soap is due†† to the simultaneous presence of

* Berichte, **35**, 2874 (1902).

† Schmatolla, Berichte, **35**, 3905 (1902); Chem. Ztg., **28**, 212 (1904).

‡ Chem. Ztg., **28**, 302 (1904).

§ Z. Chem. u. Ind. d. Kolloide, **12**, 277 (1913); **13**, 252 (1913).

‖ Z. Chem. u. Ind. d. Kolloide, **7**, 208 (1910).

¶ Pogg. Am., **141**, 44.

** Am. d. Phys., **35**, 592 (1888).

†† Stiepel, Seifensiederztg., **35**, 331, 396, 420 (1908).

soap and free fatty acid dissolved in water; these form a thin membrane about the air bubbles. According to Spring* the adsorbent action of soap towards carbon, iron oxide, clay, and similar materials plays an important part in the cleansing.

The adsorbent action is also important in the case of the long-known washing materials made from clay, and other more modern inorganic cleansing materials like magnesium hydroxide and magnesium silicate. Basic colloidal washing materials, which form insoluble soaps with fatty acids, are unsuited for use in the presence of such acids (acid oils).

Potassium salts of saturated fatty acids do (of unsaturated acids do not) show a considerable disinfecting action; the disinfecting action is not proportional to the free alkali. Cleansing action and disinfecting action run parallel in test-tube experiments† as they seem to depend on the same causes: surrounding the dirt particles and bacteria with a layer of fatty acid or acid soap. Although soaps are known which have a considerable disinfecting action in a test tube, the hands are not disinfected by such soaps by short contact (10 minutes). The number of bacteria may even be increased by washing with soap; the best disinfectants applied as soaps are more or less ineffective in their action on the skin. Alcoholic and aqueous soap solutions because of their surface tension are unable to penetrate into the capillaries of the skin. Pure alcohol because of its low surface tension is able to penetrate quickly and therefore acts as an efficient disinfectant.

V. Testing‡

(*a*) A good average sample must be taken from the inside of the soap, since the outside dries up on exposure to the air; the weighings of soap should be made rapidly to avoid the effect of atmospheric moisture.

(*b*) **Water.** 5 grams of soap are mixed with 15 grams of ignited sand (to prevent melting together) and heated 1 hour at 70° and then to constant weight at from 100° to 105°. The loss in weight gives the moisture (conventional method) in case no other volatile materials, such as turpentine or naphtha, were present in the soaps; in the latter case see page 72 for the method of Marcusson, (using a considerable amount of dry sodium chloride to prevent foaming) or determine the water by difference.

If the soap contains alcohol (transparent soap) the larger fraction of the alcohol collects in the aqueous layer under the xylol; by determining the specific gravity (Table 127), the alcohol and water contained may be calculated.

If the soap contains naphtha or other solvent material, the soap is decomposed by means of sulphuric acid, the mixture distilled, the collected hydrocarbons separated in a small separatory funnel, and then examined by the methods on page 240 and following.

* Z. Chem. u. Ind. d. Kolloide, **4**, 161 (1909); **6**, 11, 109, 164 (1910).

† Z. Hyg. u. Infectkr., **59**, (1908); **77**, 436 (1914). Seifensiederztg., **35**, 617, 641 (1908).

‡ With the assistance of J. Davidsohn.

(*c*) **Total Fat.** This is the sum of all fat-like components: fatty acids, neutral fat, rosin acids and unsaponifiable matter.

1. **Hehner Method.** The fatty acids separated from 20 grams of soap with mineral acid by the Hehner method (page 406) are weighed after washing free from mineral acid (conventional method). Water-soluble acids need be considered only in the case of cocoanut oil or palm oil soaps; in this case after adding sulphuric acid sodium chloride is added to salt out the soluble acids which are collected with the in soluble.

2. The method of Krüger* avoids the loss of fatty acids caused by a transfer from the decomposition vessel to the filter.

Five grams of soap and 5 to 10 grams of paraffin or ceresine in a weighed dish (containing a glass rod) are heated with dilute aqueous HCl till clear. After cooling, the fatty-acid cake is lifted with the rod, the aqueous solution being then run out. The cake is melted with fresh water, cooled, and washed repeatedly to remove acid. The cake is then heated with alcohol on a water bath till all water has been evaporated. The residue is then weighed. In calculating it is assumed that 100 parts by weight of fatty acid are equivalent to 96.75 parts by weight of fatty acid anhydride.

In the case of filled soaps, the added material remains in the residue in many cases. The total fat in clay soaps cannot be thus determined as the clay precipitate retains fatty acids tenaciously. Reliable results are obtained by extracting with absolute alcohol in a Soxhlet apparatus a sample of the soap rubbed up with sand. The residue (free from clay) is examined,† after distilling off the alcohol.

3. The method of Hefelmann and Steiner (see page 406), which depends on the weighing of the fatty acids as potassium salts, gives more accurate results with acids of low molecular weight (from palm oil, or cocoanut oil) than do methods 1 and 2. In drying alkali salts of linseed oil in the air, oxidations may take place, so drying in a stream of CO_2 is advised.

4. The titration method of Goldschmidt‡ is used for determining the presence of volatile acids. The fatty acids extracted by ether are not weighed; instead they are titrated, af er the molecular weight of the acids has been determined in a portion of the sample.

(*d*) The amount of soap to be obtained from 100 kilograms of fat mixture, the yield of soap, can be calculated from the amount of fatty acid contained in the soap. Thus a certain soap gave by (*c*) 62.3 per cent of fatty acid. One hundred parts of neutral fat are equivalent on the average to 95 parts of fatty acid. If 62.3 parts of fatty acid

* Chem. Ztg., **30**, 123 (1906).

† Seifenfabrikant, **36**, 493, 566, 654, 705, 739, (1916); **37**, 419 (1917).

‡ Seifenfabrikant, **24**, 201 (1904).

give 100 parts of soap, then 95 parts of fatty acid would be equivalent to 152.5 of soap. The yield of soap would be 152.5 per cent.

If the soap stock consisted of a mixture of neutral fat, fatty acids, and rosin, the ratio of these components must be known to calculate the yield of soap.

(*e*) **Free Fatty Acid.** If a soap, in cold alcohol solution, gives no red color with phenolphthalein, probably free fatty acid or unsaponified fat is present.

10 grams of soap are dissolved in neutralized 60 per cent alcohol and titrated with $\frac{N}{10}$ potassium hydroxide; the result is expressed as per cent of oleic acid (page 69).

(*f*) **Unsaponified Neutral Fat.** The total fat collected in (*c*) is titrated in alcohol solution with N/2 potassium hydroxide (phenolphthalein) and then extracted by the method of Spitz and Hönig (page 197). By evaporation of the naphtha solution, neutral fat and unsaponifiable material remain. The weighed residue is saponified with excess N/2 alcoholic potash and extracted by the method of Spitz and Hönig; the unsaponifiable matter thus obtained subtracted from the sum of neutral fat and unsaponifiable matter gives the amount of unsaponified neutral fat (conventional method).

(*g*) **Total Alkali.** This is the sum of free alkali, plus that united to carbonic acid (silicic and boric) and to fatty acids.

5 to 10 grams of soap are dissolved in water and titrated with $\frac{N}{2}$ sulphuric acid (methyl orange). From the amount of acid used, the total alkali is calculated as sodium oxide in hard soaps, as potassium oxide in soft soaps. Absence of sodium chloride and sodium sulphate is assumed. If the latter are present, an ash determination is the simplest way to get the result.

(*h*) **Free Alkali.** An excess of alkali is to be avoided not only in the case of toilet and household soaps but also in the case of soaps used to wash wool and silk, since the free alkali destroys the surface and particularly the luster of the fabrics. 0.03 per cent of Na_2O is allowed in silk-dyeing establishments; in the washing and fulling of wool for stronger woolen cloth, 1 to 1.5 per cent of alkali may be allowed.

1. **Simple Method for Determining Alkali.** Five grams of soap are dissolved in 100 c.c. of neutralized (phenolphthalein) absolute alcohol by warming, then filtered if insoluble material is present. If a red color appears in the cooled filtrate, $\frac{N}{2}$ hydrochloric acid is added to the point of decolorization (conventional method).

The appearance of a red color while hot does not necessarily point to free alkali, since even neutral soaps hydrolyze.

2. **Exact Determination of Free Alkali.** In the presence of minute quantities of free alkali, the determination of which is of of great importance in the dyeing of silk, the above method is inaccurate* because of the insufficient delicacy of phenolphthalein as an indicator in an alcoholic soap solution. The following procedure is suggested:

Five grams of soap are dissolved under a reflux condenser in 100 c.c. of 60 per cent alcohol; then excess of neutral 10 per cent $BaCl_2$ solution is added. Without filtering the precipitate of barium soap and of carbonate, the alkali is titrated with $\frac{N}{10}$ HCl in the presence of phenolphthalein.

It has also been suggested that the filtrate obtained on separating the above precipitate of barium salts be titrated by $\frac{N}{40}$ stearic acid solution.

(*i*) **Alkali Carbonate.** As a rule it is sufficient to dissolve in water† that portion of soap insoluble in absolute alcohol, to titrate with N/2 hydrochloric acid (methyl orange), and to calculate the carbonate contained from the amount of acid used; if other substances with alkaline reaction are present (borates, silicates), the carbonate is determined by weighing‡ the amount of carbon dioxide. Silicates are determined by weighing silica; borates, after previous titration of total alkali, by difference.

(*k*) **Alkali United to Fat.** An aliquot part of the fatty acids separated by (*c*) is neutralized with $\frac{N}{10}$ sodium hydroxide; from the amount of sodium hydroxide used, the total alkali united to fatty acid may be determined. This titration can also be used to determine the molecular weight of the fatty acids (page 401).

(*l*) **Nature of the Fat.** The total fat obtained by (*c*) is examined by the methods of page 380 and following. Any neutral fat and unsaponifiable matter present can be directly extracted from the soap solution with ether.

To determine the animal or vegetable origin of the fats, in case the constants of the fat lead to no definite conclusion, it is necessary to isolate the cholesterin or phytosterin from 50 to 100 grams of soap (page 398); the crude material is then further tested by page 399. Fish oil is tested for by the octobromide method (page 392).

(*m*) **Rosin.** The Morawski test is used to detect rosin qualitatively;

* Chem. Ztg., **28,** 53 (1904). Seifensiederztg., 1907. Z. angewandte Chem., **27,** 11 (1914). Seifenfabrikant, **34,** 866 (1914).

† Heermann, Chem. Ztg., **28,** 53 (1904).

‡ Finkener, Mitteilungen, **7,** 156 (1889).

quantitatively page 186 and following. According to Besson,* fats, extracted with carbon disulphide, even in the absence of rosin, will give the Liebermann-Storch reaction; wherefore if the test is positive, the iodine value and index of refraction should be determined to prove the presence of rosin.

For a quantitative determination of rosin the method of Wolff and Scholze † is used; it is more rapid than that of Holde and Marcusson. ‡ It depends on the fact (discovered by Twitchell) that fatty acids are esterified under certain conditions under which rosin acids do not react. Since by the Twitchell process some fatty acid is not esterified by the action of gaseous HCl, Holde and Marcusson combined the method with that of Gladding § in which advantage is taken of the observation that silver salts of fatty acids are insoluble in ether-alcohol while the silver salts of rosin acids are soluble. Wolff and Scholze simplify the procedure by twice esterifying with methyl alcohol and sulphuric acid.

2 to 5 grams of fatty acids are dissolved in 10 to 20 c.c. of methyl alcohol and then boiled 2 minutes under a reflux condenser with 1 volume of sulphuric acid and 4 volumes of methyl alcohol. After adding 5 to 10 volumes of 7 to 10 per cent sodium chloride solution, the mixture is extracted with ether, the aqueous layer run off and twice extracted with ether. The united ether extracts are washed with salt solution till free from mineral acid and then after addition of alcohol titrated with alcoholic $\frac{N}{2}$ KOH.

From the number (a) of c.c. of KOH and the amount of substance (m) the rosin content may be calculated: $\left[\frac{(a)\ 17.76}{m}\right] - 1.5$. The average acid value of the rosin acids is 160; 1.5 per cent is the correction for unesterified fatty acids.

After adding 1 to 2 c.c. of alcoholic KOH, the ether solution is washed with water; the wash water and soap solution are evaporated to a small bulk, acidified, and, after adding the same amount to concentrated salt solution, extracted with ether 3 times. The ether extracts are dried with anhydrous Na_2SO_4, and then the ether evaporated; the residue is dissolved in 10 c.c. of absolute alcohol and allowed to stand 2 hours at room temperature with 5 c.c. of a mixture of 1 volume sulphuric acid and 4 volumes of alcohol. After adding 7 to 10 volumes of salt solution, the mixture is extracted with ether 3 times; the ether extracts after neutralization with a few drops of alcoholic KOH are repeatedly washed with water containing a little alkali. The united aqueous-alcoholic extracts are evaporated to drive off the alcohol, then acidified, and, after adding sodium chloride, the rosin acids extracted

* Seifenfabrikant, **31,** 202 (1911).
† Chem. Ztg., **38,** 369, 382, 430 (1914).
‡ Mitteilungen, **20,** 46 (1902).
§ Williams, Analyst, **15,** 169.

by repeated treatment with ether. The ether extracts are washed with dilute salt solution, then dried with Na_2SO_4, and finally the ether evaporated. The amount of rosin acid calculated in per cent multiplied by the factor 1.07 gives the amount of colophony.

The experiments of Fahrion* show that the ethyl esters of oxy-acids are unstable, and consequently they remain unesterified; therefore in certain cases too high rosin content may be calculated. Even the double esterification does not insure a correct result when insoluble oxy-acids are observed in the ether solutions. In such a case the following method of Holde-Marcusson-Gladding is used:

0.4 to 0.6 gram of the acids (weight *b*) is dissolved in a 100 c.c. measuring cylinder (glass stoppered) in 20 c.c. of 95 per cent alcohol.

The solution thus obtained is put into a 100 c.c. measuring flask with a drop of phenolphthalein (with very dark solutions 3 drops of alkali blue 6 B are used) and enough concentrated sodium hydroxide (1 part NaOH, 2 parts of water) until just alkaline. The loosely closed cylinder is warmed for a short time on a water bath, allowed to cool, ether added to 100 c.c., the mass shaken, 1 gram of dry powdered silver nitrate added and the cylinder again shaken 15 minutes to change the acids to the silver salts. If the precipitate of the silver salts of the fatty acids has settled well (if necessary allow to stand over night), about 70 c.c. of the liquid is pipetted into another 100 c.c. cylinder (through a pleated filter if necessary). This part is shaken with 20 c.c. of dilute HCl (1 part concentrated acid, 2 parts of water) the ether layer separated and the aqueous layer again twice extracted with 20 c.c. portions of ether. The united ether extracts are shaken with 20 c.c. of water to remove acid, separated from the water, filtered into a flask and the main mass of ether is evaporated. The residue of about 10 c.c. is put into a weighed dish, evaporated, and moisture and traces of solvent are removed by short heating to from 110° to 115° till the residue has become clear and liquid.

The weight of the residue *c* is calculated to the total weight used in the Gladding method as follows (only 70 c.c. were used):

$$d = \frac{(c)\ (100)}{70} \text{ grams rosin acids.}$$

This value *d* gives the amount of rosin acids in the mixture obtained by the method of Twitchell and the amount in the original sample either directly or by simple calculation. From *d* is obtained the per cent *e* of rosin acids in the amount of original substance *a* as follows:

$$e = \frac{(d)\ (100)}{a}.$$

Since the amount of rosin acids *e* still contains some fatty acids, an average correction of 0.4 per cent should be subtracted. The unsaponifiable

* Farbenztg., 18, 1227 (1911).

matter may be considered as 8 per cent of the rosin found. The average rosin content (f) is calculated as follows:

$$f = \frac{(100)\ (e - 0.4)}{92}.$$

In the presence of more than 20 per cent of rosin it is advisable to directly determine the unsaponifiable matter; for this purpose, the ether solution of the esters after complete removal of the rosin acids, is saponified with 25 c.c. of normal alcoholic potash. The soap solution is treated with 150 c.c. of water and twice extracted with two 150 c.c. portions of ether. The main mass of the ether is distilled off and the rest evaporated at room temperature (since at higher temperatures other substances volatilize). The remaining oily residue contains only a trace of acid soaps; this is removed by treatment with a little alcoholic potash, slow evaporation of the alcohol and extraction with petroleum ether.

(n) **Inorganic Additions.** Borax, water glass, table salt, clay, chalk, etc., are to be separated by solution of the soap in alcohol; the residue is then examined in the customary manner.*

(o) **Organic Additions.** Sugar is determined polariscopically or with Fehling's solution after inversion, having previously treated the aqueous soap solution with lead acetate and sodium carbonate.

Starch remains insoluble on treating the soap with alcohol and can be qualitatively detected by touching with alcoholic iodine solution. It may be quantitatively determined by hydrolysis with dilute sulphuric acid into dextrose and then titrating this with Fehling's solution.

Gelatine is recognized by being precipitated with tannin.

Glycerine is determined, after acidification and separation of the fatty acids, in the filtrate by the acetin method (page 453).

By acidification of the solution with phosphoric acid and distillation, alcohol can be qualitatively determined by the iodoform reaction and quantitatively by determining the specific gravity of the distillate.

To determine carbolic acid and its homologues which are found in medicated soaps, use is made of the insolubility of the fatty acid salts in concentrated sodium chloride solution while the phenolates remain soluble.

100 grams of soap dissolved in hot water are treated with 10 per cent soda lye. Tar hydrocarbons are removed with ethyl ether. The alkaline liquid is treated with strong salt solution, the precipitated soap washed with salt solution, the filtrate evaporated to a small volume, washed into a measuring cylinder and enough salt added to leave some insoluble. After acidification with sulphuric acid, the volume of the separated phenols† is determined.

* Einheitsmethoden, 60.

† E. Schmidt, Pharm. Chem., **1896**, 913.

Hydrocarbons from tar and petroleum, which are sometimes added to increase the cleansing action of the soap, can be determined by extraction with ethyl ether as given above; or by solution of the soap in 50 per cent alcohol and then extracting by the method of Spitz and Hönig. In the presence of more volatile hydrocarbons, such as naphtha, 100 grams of soap are treated with dilute sulphuric acid in a roomy flask and the naphtha distilled with steam (turpentine can also be thus determined); the residue in the flask can then be saponified and tested for less volatile, unsaponifiable substances. Page 240.

(*p*) *Example of A Soap Analysis:*	*Per Cent*
Water and Bodies Volatile at 105°	38.70
Total Fatty Acid 36.21 per cent, (as fatty acid anhydride)	35.04
Combined Alkali (Na_2O), Pure Soap 39.60	4.56
K_2CO_3	3.93
Water glass ($Na_2Si_4O_9$)	13.20
Glycerine	4.01
Indifferent Salts (by difference)	0.56
	100.00

(*q*) The washing power may be estimated* by a test in the apparatus shown in Figure 132. The cloth to be tested is agitated in the apparatus. The amount of oil or soot removed may be estimated by the eye or determined by weighing the dry cloth after adding oil and soot and again after agitation in the washing device.

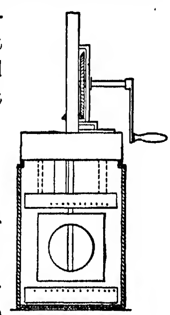


Fig. 132.

E. Soap Powder

The soap powders represent a very useful form of soap: they, however, contain many added substances, such as water glass, soda, substances liberating oxygen, etc., and small amounts of soap. The term soap powder is sometimes restricted to materials containing at least 30 per cent of fatty acid,† while products with less than this amount of fatty acids are known as washing powders.

Among oxygen-liberating substances are sodium peroxide, perborates, percarbonates and persulphates.

To test qualitatively for oxygen-liberating substances, a sample is shaken with water, dilute sulphuric acid and chloroform, and the aqueous layer separated. This

* Schiewe and Stiepel, Seifenfabrikant, **36**, 737, 754 (1916).

† Seifensiederztg., **38**, 653 (1911).

TABLE 109

Railway Specifications for Soaps in Force, 1913

Material	State	External appearance	Per cent of fatty acids	Other properties
Soft soap	Prussia, 1903	Clear and translucent, odorless	At least 40	(Brown or green soap) should be free from silica, silicates, aluminum compounds, starch and other filling material and foreign substances; should be solid at 25°. Fish oils and bad smelling oils should not be used in the manufacture of the soap. Rosin may be added but not more than 5 per cent of the weight of fat used.
	Bavaria, 1900	Light brown, translucent on the edges, of thick salve-like consistence even in summer	At least 35	Must be purest soap free from rosin, should contain no foreign caustic or weighting materials and should have the power of cleaning and lubrication. Not more than 45 per cent water, 10 per cent ash (K_2CO_3), 3.85 per cent impurities should be present. Unsaponified fat or free alkali should not be present. On storage, no liquid particles should separate.
	Saxony, 1902	Thick and viscous	At least 45	Must be prepared from linseed oil, must be free from injurious substances.
	Württemberg, 1904	Thick salve-like, viscous, light brown, translucent on the edges	At least 35	Must be the purest soap free from rosin, should contain no foreign caustic or filling materials (starch or oxides of earth metals). Must cleanse and lubricate when mixed with water and mix uniformly with luke warm water. Mineral oil and unsaponifiable fat are not allowed. Ash (aside from combined alkali) less than 5 per cent. Traces of free alkali.

TABLE 109 (*Continued*)

Soft soap	Baden, 1910	Thick salve-like, viscous, light brown, translucent at the edges	At least 35	Must be purest soap free from admixture or filling material, free from mineral oil and unsaponifiable fat, with only a trace of free alkali. On storage, no liquid particles should separate. Ash content not over 5 per cent.
	Imperial Territory, 1912	Clear and translucent, should not have a bad odor	At least 40	(Green soaps) from linseed oil without admixture of fish oils, rosin, etc. Free from impurities, additions, coloring matter. Should not crumble on storage, nor separate water, nor liquify. Should not be prepared from old, rancid oil.
White soap (curd soap)	Prussia, 1903	Should not have a noticeable odor; neither a bad odor nor artificially perfumed	At least 60	Should be a neutral curd soap, free from rosin, silica, silicates, aluminum compounds, starch and foreign materials. Lathering when used for washing. Must be dry, and should lose not more than 5 per cent of the original weight when left 5 days in the air at 20°.
	Wurttemberg, 1904	....	At least 60	(Curd soap) should be free from rosin silica, and impurities. Should be dry, water not over 25 per cent.
	Baden, 1910	Should be solid, not greasy, and should not be too dark colored	At least 60	Must be unfilled, free from foreign admixture and unsaponified fat, with traces of free alkali. Not more than 30 per cent moisture. Olein and rosin soaps not allowed.
	Imperial Territory, 1912	Not greasy, white, hard	At least 60	Must be a neutral curd soap, free from impurity, salted out, 7.5 per cent soda, not more than 30 per cent moisure, no free alkali or free fatty acid.

is covered with ether, a few drops of potassium bichromate added and then shaken; in the presence of oxygen-liberating substances the ether solution takes on a blue color due to the perchromic acid formed. See the "Einheitsmethoden," pages 66 to 70, for other qualitative methods, as well as for methods for the quantitative determination of the amount of active oxygen by direct titration with permanganate, or in the presence of ferrous ammonium sulphate.

From the following description of an analysis, the method of procedure will be understood:

A weighed amount is dried to constant weight at 105°, the moisture being thus determined. The dried powder, dissolved in water, is treated with a definite amount of $\frac{N}{2}$ HCl; the fatty acids in the soap powder are then determined by extraction with ether. The weighed fatty acids, dissolved in absolute alcohol, are titrated with $\frac{N}{2}$ NaOH, the combined alkali, and therefore the pure soap, being thus determined.

In the solution (after extracting acids by means of ether) the total alkali (calculated as Na_2O) is determined by titrating back the excess of acid with $\frac{N}{2}$ NaOH. In the neutralized solution the silicic acid of the water glass is determined by evaporation to dryness with HCl. 240 parts of silicic acid are equivalent to 302 parts of water glass or 62 parts of sodium oxide united to silicic acid.

From total alkali is subtracted the amount of alkali united with fatty acid and with silicic acid, the rest being calculated as sodium carbonate.

Summary:

Water	44.86 per cent
Total Fatty Acids (Anhydrides)	8.41
Combined Alkali (Pure Soap, 9.36 per cent)	0.95
Sodium Carbonate	39.77
Dry Water Glass ($Na_2Si_4O_9$)	4.18
Other Salts and Impurities	1.83
	100.00

F. Saponins

Saponins are often added to mixtures, containing very little soap or none at all, to increase or produce the lathering power. They are* colloidal glucosides generally soluble in water, but insoluble in ether, benzol, carbon bisulphide, chloroform, and generally in cold absolute alcohol. The formula $C_{32}H_{52}O_{17}$ is not yet definitely established. The best test is that with Millon's reagent. Saponin will produce a lather even when only one part in ten thousand is added to a soap-substitute, but this lathering power is nullified by alcohol though increased by alkali. Saponins have the power of emulsifying fat, their detergent action being due to this property.

* Weiss, Chem. Umschau, **23**, 109 (1916).

G. Wool Oils

I. General

Under wool oils are included all those oils used by manufacturers of woolens for oiling wool before spinning or rags before pulling. As such are used fatty oils, oleic acid and also emulsions of oil and oleic acid with small amounts of ammonia or soda in water, also turkey-red oils and soaps. With less valuable materials, the fatty oils may in part be replaced by mineral oils. Wool-fat oleins containing much unsaponifiable matter and the so-called water-soluble mineral oils are some of the less valuable wool oils used.

II. Requirements

Good oils should be capable of being easily removed from the fibers in the scouring process and should, during storage and working of the oiled material, develop as little heat as possible.

The best wool oils are the non-drying fatty oils, such as olive, lard and bone oils; oleic acid (olein) is also easily removed and is not likely to warm up, but is apt to attack the metal of the scribblers, which is likely later to cause spots in the fabric. Mineral oils, rosin and rosin oils are hard to remove and cause streakiness and spots in the goods for that reason; the same is true of semi-drying and drying oils, which also are liable to spontaneous combustion or likely to develop heat in the carding operations.

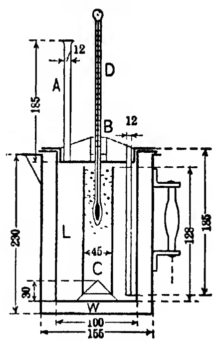


Fig. 133.

III. Inflammability

The examination should include a study of the composition (see Chapter VI) and inflammability. To determine the latter the flash point is taken according to page 38; there is also determined the rise in temperature caused by the spontaneous oxidation of the oil spread over cotton. For this test the apparatus of Fig. 133, as described by Mackey,* is used.

The apparatus consists of a metal air bath *L* heated by a water bath; through the cover is inserted a thermometer and two tubes *A* and *B* for leading air in and out. A wire gauze cylinder *C* is filled with 7 grams of cotton which has 14 grams of oil distributed over its surface; the bulb is covered with cotton. The water bath is

* Jour. Soc. Chem. Ind., **15**, 99 (1896); **35**, 454 (1916).

then kept at the boiling temperature for one hour; the temperature of the cotton is then observed. Moisture is to be carefully excluded. If the temperature is above 100°, the oil may be considered as dangerous. With very dangerous oils, the temperature may rise to 200° within 45 minutes; in case the temperature does rise above 150°, it is advisable to pull out the thermometer since the cotton catches fire very easily.

In Table 110 are given some of the rises of temperature determined by Mackey. Since the method is a comparison one, the directions must be carefully followed. The addition of metal soaps (Co, Mn, Cr, and Pb), which act as catalysts, increases the fire risk.

TABLE 110

Substance	Temperature °C. after		
	1 hr.	1 hr. 15 min.	1 hr. 30 min
9 cottonseed oils	112 to 139	177 to 242	194 to 282
8 olive oils	97 to 99	100 to 102	101 to 104
4 oleins	98 to 103	99 to 105	100 to 102 (191)
Mixture of 50 per cent cottonseed and 50 per cent olive oil	102	117	....
Mixture of 25 per cent cottonseed and 75 per cent olive oil	99	105	112
Mixture of 10 per cent cottonseed and 90 per cent olive oil	99	102	105

Others forms of apparatus have been described.* For wool-fat oleins see page 521.

H. Turkey-red Oils

I. General

To prepare turkey-red oils,† castor oil is treated with concentrated sulphuric acid below 35° and, after freeing the product from excess acid by washing with water and a solution of sodium sulphate, ammonia or soda is added till a sample gives a complete emulsion with water. In this way is obtained a yellow to brown colored oil which, according to the amount of alkali present, is soluble clear, or as an emulsion, and is used in dyeing and printing cotton with alizarin.

According to a new method‡ turkey-red oils are prepared from

* Dennstedt, Die Chemie in der Rechtspflege, 207.

† See Benedikt-Ulzer, 359, for literature.

‡ A. Grün, Ger. Patent, 260, 748, Mar. 29, 1911.

castor oil or other esters of ricinoleic acid by treatment in solution or suspension with chlorsulphonic acid, the product being dissolved in water and then neutralized; in this way not only castor oils but also acid olive oils (tournant oils) are transformed into turkey-red oils with a high content of sulphuric acid esters.

Similar products obtained by sulphonation of olive oil, peanut oil, cottonseed oil, as well as oleic acid, are considered less valuable.

II. Composition

The main components of "Turkey-red oil" obtained from castor oil are alkali salts of ricinoleic acid and ricinoleo-sulphuric acid; some neutral fat, and perhaps anhydrides of ricinoleic acid, are also present. The neutral fat is partly undecomposed glyceride; the anhydride is formed according to Tschilikin* as follows: —

$$\begin{array}{l} HO - R - COOH \\ HOOC - R - OH \end{array} \rightarrow 2\,H_2O + \begin{array}{c} O - R - CO \\ | \qquad\quad | \\ OC - R - O \end{array}$$

$$\begin{array}{l} HSO_3 - O - R - COOH \\ HOOC - R - O \cdot SO_3H \end{array} \rightarrow 2\,H_2SO_4 + \begin{array}{c} O - R - CO \\ | \qquad\quad | \\ OC - R - O \end{array}$$

The ricinoleo-sulphuric is formed by the union of sulphuric acid with the ricinoleic acid split from the castor oil, water being eliminated:

$$C_{18}H_{33}O_2 \cdot OH + H_2SO_4 \rightarrow C_{18}H_{33}O_2 \cdot OSO_3H + H_2O.$$

It is miscible with water in all proportions; the aqueous solution will lather like soap solution. The acid is precipitated from aqueous solution by sodium chloride (or hydrochloric or sulphuric acid solutions), in the form of a heavy oil (specific gravity greater than 1). By boiling with water or alkali the ricinoleo-sulphuric acid is not at all or only slightly attacked, but it is easily split into its components by heating with dilute mineral acid. Ricinoleic acid is insoluble in water; its specific gravity is less than 1. The acids separated from a turkey-red oil are denser in proportion to the amount the castor oil was sulphonated. On shaking with water, they form permanent emulsions as do the so-called water-soluble mineral oils; from the emulsion, the ricinoleic acid, which causes the cloudiness, can be extracted with ethyl ether.

Fahrion† assumes that when sulphuric acid acts on oleic acid the body first formed is an oxy-stearo-sulphuric acid, $C_{17}H_{34} \cdot OHSO_3 \cdot$-

* Lehnes Färberztg., **1914**, 419.

† Z. angewandte Chem., **27**, 596 (1914).

COOH. *Since no increase in the acid value results*, Dubovitz however considers that a di-stearo-sulphuric acid is produced, $COOH \cdot C_{17}H_{34} \cdot SO_4 \cdot C_{17}H_{34} \cdot COOH$. Fahrion seems to think the formation of a compound of stearic acid with oxy-stearo-sulphuric as very probable as such a combination would have a considerable tendency to be hydrolyzed into oxy-stearo-stearic acid and free sulphuric acid. When concentrated sulphuric acid acts on ricinoleic acid the action is stated by Fahrion to be partially a sulphonating and partly a dehydrating action. To the former is to be attributed the formation of di-ricinoleo-sulphuric acid, $SO_3OH \cdot C_{17}H_{32}COOH \cdot C_{17}H_{32} \cdot COOH$; to the latter Juillard ascribes the production of the poly-ricinoleic acids, as for example, $OH \cdot C_{17}H_{32} \cdot COO \cdot C_{17}H_{32} \cdot COOH$. These are probably the active components of the oil, as the same physical effects are obtained with oils nearly free from sulphur acids as are given by the "Turkey-red oils" rich in sulphur.

Tschilikin* claims that under 35° an ester of ricinoleic acid is formed without decomposition

$$C_{18}H_{33}(OH)O_2 + H_2SO_4 \text{ gives } C_{18}H_{33}(OHSO_3)O_2 + H_2O$$

The structure of this ester shows its tendency to form salts. The ester after careful sulphonation and standing over night can be heated to 100° without decomposition. With aqueous HCl it splits off H_2SO_4 and ricinoleic acid, and some poly-ricinoleic acid, as is shown by the saponification value. The iodine value remains unchanged; the double bonds seem to be unaltered, it is however attacked when more than 1 mole of sulphuric acid is used to sulphonate, a saturated poly-ricinoleic acid being formed which however easily splits off the added sulphuric acid residue when treated with water.

"Monopol oil" is a partially ($\frac{1}{4}$ to $\frac{1}{2}$) neutralized ricinoleic acid; it is an acid of very great emulsifying power.

The wetting ability is an important property of "Turkey-red oil" and is dependent on the presence of ricinoleic, and ricinoleo-sulphuric acids, and their salts. For many uses it is possible to prepare sulphonated oils from the free acids; in other cases the presence of neutral fat seems to be beneficial. Free ricinoleic acid is said to be more difficultly† sulphonated than is the neutral glyceride.

The calcium salt is insoluble in water, the magnesium salt is soluble. The calcium salt forms a fine emulsion in water, which separates after some time.

* Färberztg., **1914**, 419.

† Seifensiederztg., **43**, 309, 327, 342 (1916). Seifenfabrikant, **36**, 86, 108 (1916).

III. Testing

(*a*) **Solubility.** The sample must be soluble clear in a small amount of warm water and should form a permanent emulsion with 10 volumes of water. A comparison test is made with a standard oil of known purity. Both samples must react faintly acid towards litmus, otherwise they must be acidified with acetic acid. Good oils will be completely soluble in dilute ammonia, the solutions remaining clear on the addition of much water.

(*b*) **Dyeing Test.** This is an important test which should however be undertaken only by an expert; two similar pieces of cotton are soaked in a faintly alkaline solution of the oil in 10 to 20 parts of water (one in the sample, one in a comparison oil), dried, mordanted with aluminum acetate and dyed with alizarin or printed with paranitranilin red; the colors are then finished by soaping and treatment in the usual manner. The sample and the known oil are thus compared.

(*c*) **The Total Fatty Matter** determines to a large degree the value of a turkey-red oil. This value includes fatty acids, hydroxy-acids originally present in the oil or separated from the fatty sulphuric acids on heating with mineral acids, as well as neutral fat.

1. **Benedikt's Method.** Four grams of oil in 20 c.c. of water (if turbid, ammonia is added to faint alkalinity) are treated with 15 c.c. of (1:1) sulphuric acid and 8 grams of stearic acid and heated just to boiling to separate the fat; on cooling, the cake is washed free from mineral acid. From the weight of the residue the weight of the added stearic acid is subtracted.

2. The following method* has been found satisfactory:

Ten grams of oil in 50 c.c. of water are treated with 25 c.c. of dilute hydrochloric acid and boiled for 5 minutes. The mixture is then shaken with ether in a separatory funnel (ether layer 200 c.c.) and washed three times with 15 c.c. portions of water. The soluble fat and glycerine are determined in the wash water; the insoluble fat is found in the ether layer.

(*d*) **Nature of the Oil.** The iodine and the acetyl values of the total fat found in (*c*) are determined; if the first is not decidedly under 70 while the latter is 140 or higher (Lewkowitsch gives 125 as the lower limit), a pure turkey-red oil is under examination.

Only in the more exact examinations should the following tests be undertaken:

(*e*) **Neutral Fat.** Thirty grams of oil are dissolved in 50 c.c. of water, 20 c.c. of ammonia and 30 c.c. of glycerine added, and the mixture then twice extracted with 100 c.c. portions of ether. The ether solution is washed with water, then distilled, the residue being weighed after drying at 100°.

* Herbig, Chem. Revue., **13,** 243 (1906).

Herbig* determines the amount of glycerides by weighing the glycerine as follows:

8 to 10 grams are saponified with alcoholic alkali, the saponified mass evaporated to dryness on a water bath, dissolved in water, and decomposed with excess of HCl.

After complete extraction with ether, the aqueous layer is heated till all ether has evaporated, the acid is neutralized, the mass evaporated and dried one hour at 105°. The residue is pulverized and extracted 4 times with acetone, the acetone distilled, and the residue weighed at 105°. The residue consists of the glycerine united to the fatty acids, though the weight observed is only approximate, as glycerine is appreciably volatile at 105°.

(*f*) **Fatty Sulphonated Acids.** According to Herbig 4 grams of the sample and 30 c.c. of hydrochloric acid (1 : 5) are boiled under a reflux condenser for 40 minutes, shaking frequently; the clear layers are then separated on cooling by extraction of the fat layer with ethyl ether, the ether solution being then washed free from mineral acid. In the aqueous layer to which have been added the wash waters, the sulphuric acid is determined by precipitation with barium chloride. From this the amount of sulphuric acid determined in (*h*) is subtracted; the rest is calculated as ricinoleo-sulphuric acid (80 parts of sulphuric acid are equivalent to 378 parts of the ricinoleo-sulphuric acid).

(*g*) **Ammonia and Caustic Soda.** To be determined by extraction of 10 grams of oil with dilute sulphuric acid and estimation in the usual manner (see page 241).

(*h*) **Sulphuric Acid United to Alkali.** 10 grams of oil in benzol or xylol solution are shaken with a few c.c. of concentrated salt solution; in the united clear solutions, the sulphuric acid is determined.

The following shows the composition of a good turkey-red oil:

	Per cent
The water-soluble part of the fat	9.5
Insoluble part: Neutral fat	1.3
Insoluble part: Fatty acids	47.2
Total fat	58.0
Ammonia	1.8
Total sulphuric acid	4.6

I. Boiled Oils

Boiled oils are obtained:

I. By heating for several hours ("boiling") linseed oil to from 200° to 260° in the presence of inorganic lead or manganese compounds (litharge, red lead, oxides of manganese, manganese borate).

* Seifensiederztg., **42**, 164, 186 (1915).

II. By solution of 1 to 3 per cent of siccative (drying) organic salts in linseed oil at from 120° to 150°, air being blown in at the same time. These siccatives are also dissolved in turpentine and added to the cold oil. As siccatives (dryers) are used manganese rosinate and linoleate, as well as the lead and mangano-lead salts of these acids which often are the cause of a yellow or red tinge appearing. Recently cobalt linoleate, rosinate and acetate have been used since they not only increase the drying power but also exert a bleaching effect on the varnishes. In many instances zinc rosinate is used as well as salts of wood-oil and perilla-oil acids.

III. By the action of electrolytic (ozonized) oxygen on heated linseed oil, products are formed free from siccatives.

IV. Lithographic varnishes are obtained by heating linseed oil to from 250° to 300° in the absence of air and without the addition of any drying agents. The longer the oil is heated, the more viscous it becomes, the greater will be its specific gravity (up to 0.99), and the lower will be its iodine value (down to 85); finally it takes on a green fluorescence. The more the oil is heated, the more will its drying properties decrease; the glycerides largely polymerize and therefore can absorb only a little oxygen. Free fatty acids, and those liberated, are changed to anhydrides during the boiling.

EXAMINATION

Rosin, rosin oils, mineral oils, fish oils and similar oils are used as substitutes for, or to adulterate, boiled oils; soja bean oil is also added; however, only a mixture of 3 parts of boiled linseed oil and 1 part of soja bean oil gives a usable product. The following are the most important tests:

(*a*) **Drying Test.** One drop of the oil is rubbed with the finger over a 5 by 10 cm. glass plate. Good oil will be quite dry after 12 hours, often however, somewhat sticky, but completely dry after 24 hours. Poor drying points to the presence of adulterations or of raw linseed oil.

Stange* has devised an apparatus for determining the drying power of printing colors; this can also be used for varnishes.

Sand is allowed to drop from a container (*C*) (Fig. 134), moved by clockwork, upon a ½ mm. layer of the color or varnish spread over paper. At the end of a definite time the sand is brushed away from the color; the dried color or varnish however retains the sand so that it is possible to measure the distance covered with sand, and thereby estimate the drying power of the varnish. The experiment is carried out at constant temperature (35 or 45°).

* Farbenztg., **13**, 973 (1906).

(*b*) The varnishes used for printers' inks show a great variation in viscosity. Some are not more viscous than boiled linseed oil, others (such as used for gold-lettering) may be very viscous. The viscosity is recognized as being of great importance in determining the usefulness of these materials, so that a variety of analytical methods have been suggested.

The viscosimeter method of Engler has not been satisfactory because of the long time of efflux, and because most varnishes contain thickened portions which influence the time of out-flow and therefore cause uncertain results.

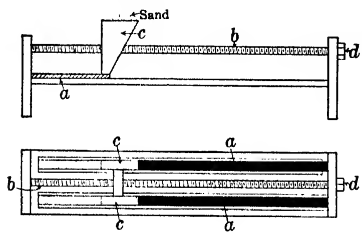


Fig. 134

The crudest test depends on the feel of the varnish. A comparison is made between a previously satisfactory sample and the one under examination. With sufficient practice this method will yield satisfactory conclusions.

Another simple test consists in filling two similar glass tubes, one with the sample, the other with a comparison material previously found satisfactory; by tilting the tubes, the time of outflow is compared and therefore an approximate idea of their relative viscosities is obtained.

Better is the method depending on the principle of a rising air bubble; the time necessary for a bubble of constant size to rise through a definite length of varnish is measured. The method is quite satisfactory with less viscous materials provided sufficient observations are made to get an average value; with more viscous samples, the easy change in the form of the bubbles causes inaccuracies.

Valenta* has described a method in which a 9 mm. silver sphere is allowed to drop vertically through a definite length of varnish placed in a burette of 13 mm. diameter. The viscosity is assumed proportional to the time of fall through a given distance.

In this method the sphere of silver remains unaltered in size; an air bubble under the same conditions would be constantly changing its form. The ball, however, may not drop exactly in the centre of the burette; since the resistance is less along the sides, the time of fall is not constant, though on many repetitions a good average value is obtainable.

A more complicated method devised by Stange has already been described on page 10. This is suited to the most accurate determinations.

* Chem. Ztg., 30, 583 (1906).

(*c*) **The Specific Gravity,** as a rule, lies between 0.935 and 0.948. Mineral oils, fish oils and other fatty oils lower the specific gravity, while rosin oils increase it; thick boiled oils may have a specific gravity as high as 0.99 (sometimes higher).

(*d*) **Iodine Value.** 150 to 172 is the ordinary range; the value is lower the longer the heating and the longer the action of oxygen.

A low iodine value is generally found in dark oils; the highest values in light-colored oils are in general found in those oils prepared at lower temperatures. With very thick boiled oils the iodine value may drop to 70. Regarding the hexabromide value of linseed oils and boiled oils see page 415.

(*e*) **Saponification Value.** 190 to 195 as in the case of linseed oil itself.

(*f*) **Unsaponifiable Matter.** The natural amount present in linseed oil (about one per cent) is not increased by boiling. See page 76 for its qualitative detection and page 197 for the quantitative determination. In doubtful cases the iodine value of the unsaponifiable matter is determined; the natural unsaponifiables (phytosterin, etc.) have a value between 60 and 70, in mineral oils a maximum of 15 (see page 388).

The Morawski qualitative test for rosin oil (page 186) is unreliable since pure boiled oils give a similar color reaction.

Besides rosin oil and heavy mineral oils, turpentine oil or mixtures of naphtha or kerosene with a little turpentine are added to boiled oils. In this case the method of Spitz and Hönig would give too low results for unsaponifiable matter, because of evaporation; the correct value can be calculated from the saponification value. The volatile oils can be directly determined by distillation over a free flame or by distillation with steam; in the distillate the turpentine or naphtha can be detected by odor, optical rotatory power, bromine absorption and tests given on page 319.

(*g*) **Dryers. Siccatives.** By extraction of an ether solution of the oil with dilute nitric acid and examining the acid extract, or by ashing a sample and analyzing this, the basic radicals present may be determined. Lead and manganese occur most frequently; cobalt, zinc, calcium less often. Manganese is determined easily by fusion with a mixture of sodium carbonate and nitrate (green color). Quantitative determination is generally unnecessary. If the quantity is to be determined, 20 grams of oil in 50 c.c. ether, in the presence of methyl orange and water (30 c.c.), is treated hot with $\frac{N}{2}$ hydrochloric acid drop by drop until after continued shaking the aqueous layer remains red. From the amount of acid used the amount of siccative salt can be calculated (the molecular weight of the rosin acids is taken as 346) the acids being assumed mono-basic.

(*h*) **Free Acid** is determined in connection with (*g*). The ether solution and the aqueous layer just acidified with hydrochloric acid is titrated after adding alcohol

and phenolphthalein. From the amount of sodium hydroxide used the quantity equivalent to the hydrochloric acid (in *g*) is subtracted; the difference corresponds to the amount of free organic acid present in the boiled oil. In direct titration of the oil with sodium hydroxide an error may arise in that the sodium hydroxide may not only unite with the free acid but may decompose some of the siccative salts.

(*i*) **Rosin.** Small amounts of free rosin can be detected, in oils prepared by the addition of salts or rosin acids, by extraction with 70 per cent alcohol (page 186); only when, by this method, considerable amounts of resinous extract are obtained, does it point to adulteration with rosin. Since manganese and lead rosinates are somewhat soluble in 70 per cent alcohol, their amount is to be determined, by ashing the extract or by titration with $\frac{N}{2}$ hydrochloric acid, and deducted from the amount of rosin found. A large amount is made evident in the acid determination; rosin-free boiled oils seldom have an acidity of more than 12 and generally only 7. Free rosin raises the acidity considerably. See page 471 for quantitative determination. The Morawski test is not always reliable (see (*e*) above, also page 429).

EXAMPLE

An oil was to be tested to determine if it was a raw or a boiled oil, and if free from additions.

The oil had the odor of linseed oil, was yellow, mobile, cloudy; specific gravity at 15°, 0.9376. Unsaponifiable matter absent. Water present caused the turbidity, it disappearing on warming but reappearing on cooling. Waller iodine value, 166; saponification value, 197. Siccative, about 2 per cent of mangano-lead rosinate. After 15 hours at room temperature it was dry; after 2 hours at 50°, it dried to a solid non-sticky covering. The material was evidently a boiled oil prepared by gentle warming and with the addition of 2 per cent of mangano-lead rosinate. Additions absent.

The acid value of ten oils of normal composition tested in the Royal Materialprüfungsamt gave values between 1.2 and 3.6 calculated as oleic acid (or 2.4 to 7.3, as acid value). Two oils containing free rosin had an acid value of 14.6 and 14.8 (equivalent to 7.3 and 7.4 per cent oleic acid), corresponding to 9.4 and 9.5 per cent of rosin calculated as colophony.

TABLE 111

RAILWAY SPECIFICATIONS FOR DRYERS AND VARNISH (IN FORCE, 1913)

	State	External appearance	Specific gravity at 15°	Other properties
Varnish	Prussia, 1901	....	. .	Must be prepared from pure linseed oil, with the addition of manganese or lead compounds, free from admixed material and should give no sediment on long storage. Painted in a thin film on glass plates it should show after 18 hours at 20° a dry, not sticky surface which does not darken.
	Saxony, 1901	Must have a clear appearance and must retain it	At least 0 940	To be prepared from pure fatty linseed oil, twice boiled, without admixture of other vegetable oils, or rosin oils, completely settled, no sediment. It should dry quickly.
	Württemberg, 1904	Light colored, odor and taste of linseed oil, not a burnt odor or unpleasant	0 935–0 943	From the purest, settled linseed oil, must retain luster on drying. Should give no sediment on standing, the color should be according to use of oxidizing agents (lead or manganese derivatives), clear translucent, reddish yellow to red brown, dark brown and black are excluded. After 48 hours dried. Free from rosin, rosin oil, hemp-seed oil, rape oil and fish oils.
	Imperial Territory, 1912	Light colored and transparent	. ...	Pure, free from slime and sediment, well dried and settled. Painted on lead plates, dry after 24 hours at 15°. Waterproof varnish to be prepared from pure linseed oil with the addition of lead-manganese compounds, free from foreign bodies (rosin, rosin oil, linseed oil, fish oils). Dried after 15 hours at 15°.
Dryers	Prussia, 1901	....	. .. .	To be delivered in clear solution, free from foreign admixture; it should give no sediment on standing. Brushed over glass plates, it should no longer be sticky after 10 minutes at 20°, and should be hard after 2 hours.
	Saxony, 1901	Must have and retain a clear appearance	. ...	To be prepared from pure linseed and turpentine oils, without admixture of rosin oils or vegetable oils, well settled and giving no sediment on standing. Mixed with the varnish colors, it should dry well and adhere firmly.
	Imperial Territory, 1912	....	.....	Must dry in 5 minutes at 15°.

K. Paints and Putty

Paints are prepared by grinding up an inorganic pigment (white lead, zinc white, lithopone, iron oxide) with drying fatty oils, such as linseed oil, or boiled oil, poppy-seed oil, or substitutes.

Putty is made by mixing precipitated chalk with raw linseed oil, or boiled oil, or substitutes; the linseed oil is often replaced in part by mineral oil to cheapen the binding material and to prevent too rapid drying which may cause cracking. At times, graphite, pyrolusite, red lead, or even asphalt* may be added. To hasten its drying litharge, zinc white, manganese borate or other bodies may be added. To increase the plasticity castor oil is sometimes added.

For optical instruments lead glycerinate is often used as a cement. Glycerine is rubbed together with litharge; this hardens in a few hours. A mixture of 75 per cent litharge and 25 per cent of glycol† hardens even more rapidly; the speed of hardening is decreased by decreasing the amount of glycol.

ANALYSIS

A weighed sample of the oil must first be separated from the pigment by extraction with successive portions of ether by decantation, or, if the pigment does not settle easily, petroleum ether is used; the liquid is poured through a filter paper. The siccative (dryer) can then be extracted with ether. A clear separation of pigment and oil suspended in ether is obtained by use of a centrifuge.

If only the oil, and not the pigment, is to be examined, a weighed sample can be shaken in a separatory funnel with ether and an excess of dilute hydrochloric acid (at times a little alcohol may be added); after settling, the ether is run off and filtered. The extraction is repeated. On evaporation of the ether, the binding material, rosin, and fatty acids from the decomposition of the dryer will be found in the residue. The oily material is then further examined by the methods described in Chapter VI, page 385.

The examination of the oily portion is made as described under oil varnishes on page 319. If a volatile solvent is present in the paint (turpentine) this is separated by distillation with steam, the distillate being examined by itself. The residue is sucked dry and free from water and then treated with ether as described.

To examine putty containing asphalt, the undried linseed oil is

* D R. P. 154, 220.

† D. R. P. 302, 852.

extracted, the asphalt then removed by treatment with chloroform and the residue dissolved with warm alcoholic potash, which dissolves the insoluble oxidation products of linseed oil. The testing of the separated components is then carried on as described previously.

L. Varnishes and Components

Spirit varnishes are solutions of different resins, such as shellac, copal, amber, asphalt, colophony and salts of rosin acids in volatile solvents, like alcohol, turpentine, amyl alcohol, amyl acetate, acetone, naphtha and coal-tar oils; oil varnishes contain, besides the substances mentioned, linseed oil or boiled oil, rosin oil, etc.

The chemical examination of such varnishes is often very difficult, since the methods for the varied substances, in the presence of each other, are inadequate; the resins are often not present in their original condition, because of previous prolonged heating. A method of analysis applicable to all cases cannot be given.

I. Mechanical Testing

(*a*) The drying power of a varnish or the hardness in thin films is tested by the nail test or in the Clemens apparatus (Fig. 135). The scratches or marks made by the finger nail or by the knife edge on the

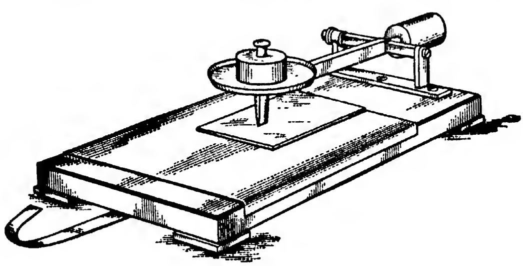


Fig. 135.

dried varnish are examined. The material is judged by the character of the marks (splintering, etc.) and by the size of the weight which must be applied to cause the marks.

(*b*) **The Elasticity of the Varnish** is determined by covering a piece of thin metal, allowing to dry, and then bending 90° and then 145°, to determine if the varnish film has cracked. Certain artificial resins (from phenol and formaldehyde) meet this test as well as the copal resins.

II. Resistance to Alkali

This property is of importance under certain circumstances and is determined by noting the resistance to soda and ammonia solutions.

15 to 30 per cent sodium carbonate solutions are allowed to act on varnished glass plates for 3 hours at room temperature, the liquid is then heated slowly for 35 min. to 80° or 90°, or quickly in 6 minutes to boiling. After remaining for some time in cold 30 per cent soda solution, the film is examined. If it does not dissolve on spraying with water, the varnish may be considered acceptable. If the color changed to brownish-yellow, then some of the film will probably dissolve; such a varnish is unsatisfactory.

In determining the resistance to ammonia, a varnished glass plate is moistened with 10 to 12.5 per cent ammonia solution, and allowed to react for several hours under a bell-jar. If only a small dullness develops, the varnish is resistant enough to use. If the film can be loosened by gentle rubbing with a glass rod, then the varnish should be considered unsatisfactory. A good varnish should not loose its lustre or color, nor be loosened from its support, after being exposed to the action of ammonia gas for 15 minutes.

III. Chemical Examination

(*a*) **Volatile Solvents.** A large sample (50 to 100 grams) is distilled with steam till no more oil passes; the distillate can be caught in a flask (shown in Fig. 118, page 267) of 1 liter capacity and with graduated neck, the volume being read directly; or it may be caught in a separatory funnel, sodium chloride added, to allow an easier separation of the two layers, the oily layer being filtered through a dry filter and then weighed.

The examination of the varnish then will consist of the testing of the distillate and the residue. If acetone or alcohol is present in the varnish, these being soluble in water, a separation is made by direct heating instead of by steam distillation, the material being heated to about 200° in an oil bath. A higher temperature should be avoided to prevent decomposition of linseed oil, etc.

Alcohol and acetone differ from the other volatile solvents present in varnishes in being soluble in water; alcohol is recognized by the iodoform test (page 240). Acetone can be detected through its boiling point, or by its reaction with hydroxylamine or with phenylhydrazine. Amyl alcohol and acetate are recognized by their characteristic odors, the latter by forming acetic acid on saponification.

Tests for turpentine and substitutes, naphtha, benzol, pine oil, rosin spirits, etc., are given on page 319.

(*b*) **Non-Volatile Components.** In the examination of varnishes, the resin as well as the solvent must be considered; either the undissolved resin or its solution in turpentine, alcohol, etc., (spirit varnish), or a mixture with drying fatty oil (oil varnish) is to be tested. In the former case an examination is made on the basis of the values recorded in Table 112 on page 494; in the latter case after distilling off the solvent, the resins are separated from the fatty oil by proper solvents or precipitation reagents.*

In the examination of these materials the appearance of the residue from steam distillation gives valuable hints. At first tests are made for salts of resin acids (lead, manganese and calcium); a portion of the sample is ashed, the residue being examined by the regular procedures of qualitative and quantitative analysis.

Colophony is detected by the blue-violet color in the Morawski reaction; all other resins give an uncertain red or brown tint. The recognition of the other resins is accomplished by help of Table 112, but it must be remembered that frequently they are no longer present in their original condition, since in the manufacture of the varnish they have been melted, hardened, etc., into other bodies with entirely different properties. Besides the resins described in the table, there are at times found synthetic preparations, page 497, (for example, bakelite, a condensation product of phenols and formaldehyde, glyceryl esters of resin acids, etc.).

If an oil varnish is under examination, this is made evident in the steam distillation, in that the residue is thick and oily.

To test for dryers (Pb, Zn, Mu, Co, Ca), the material is ashed, or the residue from the steam distillation treated with naphtha and hydrochloric acid (see page 486).

Free resin is tested for by means of the acid value (page 69, or in the presence of dryers according to page 487); a low acid value (under 1) means absence of free resin. The naphtha extract is qualitatively tested for unsaponifiable matter, and if unsaponifiables are present, tested for mineral oil and rosin oil (pages 76 and 119). The fatty residue (according to Spitz and Hönig) is then tested according to page 385 and following, taking account of the change in property of linseed oil on boiling.

1. Natural Resins

According to Holde, the solubility of colophony in cold acetic anhydride allows the easy detection of colophony in the presence of other resins, for on adding a drop of sulphuric acid (1.53) a blue-violet color appears in the presence of colophony.

(*a*) **Determination of the acid value of resins.** The characteristic acid values of resins serve to determine their purity. It was formerly determined by dissolving the resin in a proper solvent and then titrating with $\frac{N}{10}$ alkali as in the determination of the acid value of fats.

*See H. Wolff, Farbenztg., **16,** 2056 (1911); Zimmer, ibid., **17,** 456 (1911).

TABLE

PROPERTIES

D = Dieterich. S. and E. = Schmidt and Erban. M. and W. = Marcusson

(Values found by M. and W.

	Kind of resin	Liebermann-Morawski reaction	Acid number of the resin (direct)	Ester number of the resin	Saponification value of the resin	Iodine value ††
1	Colophony (main component abietic acid, $C_{20}H_{30}O_2$)	Dark blue or red violet at once	140 to 180 D. 146 * 151 Kr.	8 to 36 22 *	167 to 194 146 6 *	115 to 117 *
2	Shellac (main component resinotannol ester of aleuritic acid)	Dissolved cold no color, dissolved warm, no characteristic color Hd. and M.	65 5 Kr. 63 * 60.8 to 64.4 P.S.†	136 to 163 ‡ 50 2 Kr. 150 * 138.5 to 141.6 P.S.	194 to 212 ‡ 208 * 201 to 203.6 P.S.	0 to 6 * [8] [8 2 to 9 6] P.S.
3	Amber (main component succinoresinol ester of succinic acid)	Dissolved cold, colorless to faint red, dissolved warm, violet red. Heated amber, dissolved cold gives rose color slowly. Hd. & M.	15 to 35 D. 33 to 34 Kr. 15 5 to 33 §	71 to 91 74 5 to 91.1 Kr. 106 to 112 §	86 to 145 145 * 127 to 137 §	....
4	Copals: Zanzibar copal (main component trachylolic acid)	Brown Hd.	35 to 95 D. 80 to 85 Kr. 71 §	12 §	91 * 83 §	....
	Copals: Kauri copal	Reddish	66 §	8 §	74 §	....
	Copals: Manila copal	Brown	136 142 §	42 § 52	188 ‡ 184 §	....
5	Dammar (main components dammarolic acid and dammarresene)	Red Hd. & M.	31 to 34 Kr. 20 to 35 D. 32 * 25 §	15 * 9 §	42 §	....
6	Sandarac (main component sandaracinolic acid)	Brown	95 to 155 D. 140 * 144 Kr. 138 §	32 * 40 §	167 5 * 178 §	64 to 67 *
7	Mastic (main component masticin)	Brown red	50 to 70 D. 64 * 60 § 62(71) Kr.	55 § 23 to 29 29 *	106 § 73 to 93 93 *	....
8	Elemi	....	18 to 24	6 to 46	25 to 68	....

* S. and E. † Puran Singh, J. Soc. Chem. Ind., **1910**, 1435.

‡ Williams. § M. and W.

|| Strongly distilled amber (40 to 45 per cent distilled) is easily soluble in hot cajeput oil and is not precipitated from this solution by the addition of naphtha boiling below 50°.

112

OF RESINS **

and Winterfeld. Hd. = Holde. P.S. = Puran Singh. C. = Coffignier. Kr. = Kremel.
were determined in benzol-alcohol solution)

Solubility in: Alcohol, 70 per cent	Alcohol, Absolute	Ether	Acetic anhydride (Hd.)	Cajeput oil	Acetone	Petroleum ether	Turpentine	Other observations
Soluble	Soluble	Soluble	Easily soluble cold		Soluble	Nearly all soluble	Soluble	. .
..	Same 0 6 to 1 1 per cent insoluble (P.S.)	Insoluble	Very little soluble cold, easily soluble warm		Almost insoluble	Insoluble	Almost insoluble	Acids can be esterfied with alcoholic hydrochloric acid; difference from other resins.
Insoluble	Almost insoluble	Little soluble	Almost insoluble cold, little soluble warm	Little soluble ‖ W.	Little soluble	Little soluble	Partially soluble	Acid value of the separated acids 93.§
Same	Natural insoluble, skinned almost all soluble	Partially soluble	Little soluble cold, partially soluble warm	Almost completely soluble when heated ¶	Insoluble	Insoluble	The same	..
. .		More easily soluble than Zanzibar copal	Little soluble cold, completely warm, part precipitating on cooling	The same ¶ W.			More easily than soluble Zanzibar copal	. .
...	-	The same	Little soluble cold, almost all soluble warm	The same ¶ W.			The same	.
....	Partially soluble 19 to 45 per cent C.	Soluble	Little soluble cold. partially soluble warm		Largely soluble	Soluble	Soluble	
....	Soluble	Same	Little soluble cold, almost completely soluble warm	. .	Soluble			Insoluble in benzol.
....	Partially soluble	Same	Little soluble cold, almost all soluble warm	..	Partially soluble	Insoluble	Partially soluble	.. ...
...	Soluble	Same		.	Soluble	Soluble	Soluble	..

¶ Is precipitated from solution by the addition of naphtha boiling below 50°.

** See also Rebs (Chem. Rev., 1912, 155) regarding solubility of the different resins in conc. acetic acid, in naphtha, sal ammoniac, etc.

†† The values in square brackets by determining the iodine value of the alcohol-soluble and insoluble portion together; the other values are for the parts soluble in alcohol.

K. Dieterich later proposed the method of titrating back, a weighed amount of the resin being treated with an excess of alkali and then the unused alkali determined by titration; this suggestion was made because some of the resins did not dissolve in the customary solvents, and also because the free resin acids combined with the dilute alkali only slowly. It has been shown* that anhydrides, phenol acids and lactones† are also present in resins (for example colophony) and these are gradually attacked by dilute alkalies. The method of titrating back therefore gives widely divergent results, depending on the time of reaction and the strength of the alcoholic alkali.

The following method has therefore been suggested by Marcusson and Winterfeld:‡

4 grams of the powdered resin are dissolved in 200 c.c. of a mixture of benzol and absolute alcohol, and after cooling, without filtration, titrated with $\frac{N}{10}$ alkali; since phenolphthalein does not give a sharp end point in the presence of shellac, alkali blue 6b is used.

The value for the copal was in one case, 72.8, in the other, 72.4; for the dammar resin in both cases 24.8.

(*b*) Determination of Free Acid in Presence of Soaps

If ammonia soap is present in resins, in water-soluble rosin oils and in mineral oils, the ammonia is separately determined by the method of page 241. The amount of combined resin acid thus determined is subtracted from the total determined by titration.

Calcium resinates are added to the colophony to harden it. In titrating such material in benzol-alcohol solution with alkali, at first a basic calcium soap will form which does not dissociate, nor react with phenolphthalein; the material is therefore diluted with water till the alcohol is 50 per cent and the solution will react with the indicator, or the procedure given under lubricating greases (page 228) is used.

In the presence of aluminum, iron, manganese and lead soaps, basic salts are obtained which do not dissociate even in presence of water.

These can be estimated by the method of Holde in which 15 grams are dissolved in 50 c.c. of benzol, filtered and 30 c.c. of water containing methyl orange added; the benzol solution is then titrated hot with $\frac{N}{2}$ hydrochloric acid, the end point

* Henriques, Ztschr. f. angew. Chem., **12**, 106 (1899).

† Fahrion, ibid., **14**, 1197, 1221 (1901).

‡ Chem. Rev., **16**, 104 (1909).

being sharper if some methyl orange is added after decomposition of most of the soap. The aqueous layer is separated, the oil layer washed free from mineral acid, neutral alcohol added and then titrated with $\frac{N}{10}$ alkali in presence of phenolphthalein. From the difference in the two titrations the amount of free acid may be calculated.

Marcusson and Winterfeld* have described the special testing of amber substitutes. Amber is a fossil resin of Pinus succinifera and contains as the main component succinic acid ester.† It has a specific gravity 1.05 to 1.096, a hardness 2 to 3, and a melting point of from 250 to 300°.

Of its substitutes celluloid can be recognized by its strong solubility in glacial acetic acid, high nitrogen content, and easy combustibility. Colophony can be easily recognized by its solubility in 70 per cent alcohol and the Morawski reaction.

Most like amber is copal, especially the hard Zanzibar copal, which is a fossil resin of deciduous trees (the copal trees). On distillation it gives no succinic acid (amber does); however, it is not easy to distinguish between amber and copal by this test, though amber yields from 3 to 8 per cent succinic acid.

Another method allows separation by solubility in cajeput oil. Zanzibar copal is almost completely soluble in this oil, 14 per cent of amber is insoluble. By adding naphtha to the solution, a definite precipitate forms in the case of the Zanzibar copal, amber gives only a cloudiness. The test is performed as follows: —

2 grams of the finely powdered resin in 25 c.c. of cajeput oil is boiled 10 minutes under a reflux condenser, then any insoluble matter filtered off, and heavy naphtha added to the filtrate. In the presence of 10 per cent copal a precipitate will form; this is true of Zanzibar, Kauri, Manila, Congo, Leone, and Brazil copals, as well as St. Domingo amber, which is really a copal.

2. Artificial Resins

Ordinary rosin is made more valuable by giving it a higher melting point, so that it no longer will stick to the hand. For this purpose salts and esters of colophony have been prepared which have in addition the advantage of not separating from drying fatty oils, turpentine, etc., and furthermore can be mixed with metal pigments (such as white lead or zinc white) without forming hard compounds. Rosin esters have been prepared from alcohols, phenols, naphthols, and from car-

* Kunststoffe, I, 281 (1911).

† Dieterich, Analyse der Harze, **1900**, 95.

bohydrates by removal of water; they are insoluble in soda, and may be prepared, also as glycerin esters, in various degrees of hardness. They however form very slowly drying varnishes, quite unsuited, for chairs, for example. Such esters are too expensive to be substituted for calcium resinate, and are not as resistant to weather as the copals, so that their application is somewhat limited.

With the outbreak in the war, in Germany all linseed oil and other materials used for the production of varnishes and paints were of necessity replaced by various domestic substitutes.

M. Rosin Size

I. General

To prevent ink from spreading during writing or printing, the paper must be sized or coated on the surface; this also gives the paper greater resistance, a better feel, and a better color. Before the war rosin size was used to a large extent; it was generally a mixture of alkali resinate and free rosin, obtained by boiling colophony with an amount of sodium carbonate or hydroxide insufficient for complete reaction. The paper is sized by adding the rosin soap in the hollander, and after beating, introducing a solution of alum or aluminum sulphate, whereby insoluble aluminum compounds are formed which drag down free rosin and produce the size. During the war various substitutes, including saponified montan wax and aluminum formate, were used in Germany for sizing paper.

II. Analytical

The following procedure* is satisfactory with ordinary sizes prepared from rosin.

For an average sample the size is heated till liquid and then thoroughly mixed.

2 to 3 grams of rosin size in 20 c.c. of hot water are treated in a separatory funnel with 50 c.c. of $\frac{N}{10}$ sulphuric acid. The separated resin is extracted with ether, the lower aqueous layer is run into a larger separatory funnel, the ether solution is washed several times with water, and the washings added to the original water layer. The combined aqueous mixture is then again shaken with ether, and is then run into a flask to titrate back excess of sulphuric acid with $\frac{N}{10}$ sodium hydroxide. If (n) c.c. of alkali were used, then $50 - n$ c.c. of acid were necessary for the neu-

* Dalen, Chem. Technologie des Papiers, Leipzig, 1911.

tralization of the alkali in the rosin soap. The composition of the soap is calculated as follows: —

$(50 - n)\ (0.0031)$ = amount of alkali, calculated as Na_2O

$(50 - n)\ (0.0302)$ = amount of combined rosin acid (molecular weight = 302) calculated as acid.

$(50 - n)\ (0.0293)$ = amount of combined rosin acid, calculated as anhydride.

To determine the free acid and the unsaponifiable rosin components, the united ether extracts are titrated, in the presence of phenolphthalein, with $\frac{N}{10}$ alkali. If (m) c.c. of alkali are used for the titration of the total rosin, since 1 c.c. of $\frac{N}{10}$ alkali is equivalent to 0.034 grams of rosin (acid plus unsaponifiable matter):

$(m)\ (0.034)$ = total rosin

$(m)\ (0.0302)$ = rosin acids

$(m)\ (0.034 - 0.0302) = (m)\ (0.0038)$ = unsaponifiable matter

$(0.0302)\ (m + n - 50)$ = free rosin acid present.

The composition is therefore: alkali (calculated as Na_2O), combined rosin (calculated as anhydride), free rosin (acid plus unsaponifiable), water, and impurities. The water can either be calculated by difference, or determined by distillation with xylol according to page 72.

In the case of rosin size for better papers, which must not become yellow, fatty acid soaps (oil and stearic acid soaps) may be present; in this case the rosin must be gravimetrically determined by the method of page 471.

The above-mentioned procedure is not applicable when other sizing materials such as animal glue, mucilage, casein, albumin, starch, dextrin, gum arabic, viscose, or gluten may be present. Marcusson* suggests the following procedure:

Ordinary rosin size dissolves in cold alcohol, all of the mentioned substitutes are insoluble in alcohol so that they may be quantitatively separated and determined. A portion of the alcohol-insoluble material is ashed, as sometimes inorganic loading materials like kaolin, barium sulphate, etc., are added. The ash-free material is examined by page 77 for nitrogen; if nitrogen is absent, then it is unnecessary to look for animal glue, albumin, or casein. Starch is identified by its characteristic appearance under the microscope, and by the blue color produced on adding iodine solution. Starch, if it is not soluble starch, can be separated from dextrin and gum arabic by its slight solubility in cold water. Soluble starch need hardly be expected. To distinguish between dextrin and gum arabic advantage is taken of their difference in behavior towards lead acetate; gum arabic is precipitated as a flocculent mass, dextrin remains in solution and can be recognized by its decided dextro-rotatory power ($(\alpha)_D = +216°$). Viscose (alkali cellulose-xanthogenate) is decomposed by treatment with dilute mineral acids into hydrogen sulphide and cellulose.

Mitteilungen, **31**, 457 (1913).

Mucilages *(flax seed)* are not often added to rosin size; on the addition of alcohol a threadlike flocculent precipitate, clumping together, will form, which in aqueous solution will give a precipitate with lead acetate. Mucilages are distinguished from gum arabic by the precipitates given with 5 per cent tannic acid solutions; gum arabic is precipitated by lead acetate but not by tannic acid.

If the alcohol insoluble portion of the size contains nitrogen, animal glue must first be suspected. Such glue is not precipitated from solution by acetic acid either hot or cold; but tannic causes a precipitate (page 74). On warming with alkaline plumbite solution no lead sulphide forms with glue, but a black precipitate does form in the case of mucilage, albumin, and casein. Albumin is soluble in cold water, is precipitated on warming and on the addition of acetic acid. Gluten and casein are soluble only as alkali derivatives in water and are reprecipitated on addition of acetic acid. Casein is distinguished by its high content of phosphorus (0.8 per cent) and its precipitation by rennet.

If nitrogen compounds are present, non-nitrogenous sizes may still be present, such as dextrin, starch, and gum arabic. Starch is easily identified by the iodine reaction, and dextrin and gum arabic are tested for after the nitrogen-containing glue has been precipitated by tannin and then filtered.

N. Blown Oils

I. General

By blowing air into rapeseed and cottonseed oils heated to 120° very viscous products of the consistency of castor oil are obtained; these differ from the latter, however, by being soluble in naphtha and in mineral lubricating oils, as well as in being difficultly soluble in alcohol. They are sometimes known as soluble castor oils, blown oils, or thickened oils, and come on the market mixed with mineral oils as lubricants in so-called marine oils. The color of these oils is lighter, the lower the temperature of blowing. By the action of oxygen of the air, a part of the unsaturated acids is changed to naphtha-insoluble oxy-acids; another part decomposes into volatile acids of low molecular weight; a considerable amount of polymerization, as well as lactone formation, occurs. Consequently the viscosity, specific gravity, Reichert-Meissl value, saponification value and acetyl value increase and the increases are the greater, the higher the temperature of blowing; in corresponding degree, the iodine value sinks.

The properties of some blown oils are given in Table 113; for the sake of comparison, the properties of rapeseed and of cottonseed oils are also given.

II. Examination

(*a*) **Differences Between Oils.** It is extremely difficult to distinguish between different blown oils, since the constants have such a wide range, and as may be seen from the table, they may be the same

for rape and cottonseed oils. Furthermore the color reactions fail. Blown cottonseed oils do not give either the Halphen or the Milliau tests; it is true the nitric acid test is given, but it is also given by rape oil. To distinguish between them the following tests are of some value:

TABLE 113

PROPERTIES OF PURE AND BLOWN RAPE AND COTTONSEED OILS

	Specific gravity at 15° C.	Iodine value	Saponification value	Reichert-Meissl value	Per cent oxy-acids insoluble in petroleum ether
Pure rape oils. . .	0.913 to 0.917	94 to 106	170 to 179	0.3	0
Commercial blown rape oils (examined at the Materialprufungsamt)	0.968 to 0.975	47 to 52	209 to 217	3.8 to 4.4	24 to 27
Commercial blown rape oils (Lewkowitsch) . .	0.967 to 0.977	47 to 65	198 to 267 (175)	To 8.8	20.7 to 24.9
Pure cottonseed oils	0.922 to 0.925	108 to 110	191 to 198	. . ..	0
Commercial blown cottonseed oils (Lewkowitsch) . .	0.972 to 0.979	56 to 65	214 to 225	. . ..	26 to 29

1. The odor resembles that of the unblown oil.

2. The consistence of the fatty acids. The fatty acids of blown rape oil (erucic, oleic and rapic, besides small amounts of palmitic, stearic and arachidic acids) because of their pronounced unsaturated character are oily; the acids separated from blown cottonseed oil, because of the presence of considerable amounts of saturated acids (palmitic and stearic acids), are of the consistency of tallow (melting point 54 to 59°).

3. Behavior of the lead soaps in presence of ethyl ether. Corresponding to the different composition of the acids, mentioned under 2, the lead soaps of rape oil acids are more soluble in ether, dissolving almost completely; while those of cottonseed oil remain largely undissolved. Marcusson* has based a qualitative test for distinguishing between blown rape and blown cottonseed oils on this property:

The acids are liberated from the oil in question and separated into those soluble in petroleum ether, and those insoluble. The lead salts of the petroleum ether-soluble portion (see page 371) are then prepared. In the presence of blown rape

* Chem. Rev., **16**, 45 (1909).

oil, the lead soaps are completely soluble in warm ether and on cooling only traces separate. If cottonseed oil is present, a considerable amount (14 to 18 per cent) remains undissolved.

(*b*) **Mixtures of Mineral Oil and Blown Oils.** The following tests are made to determine whether blown oils are present in a mixture of fatty oil and mineral oil:

TABLE

EXAMINATION OF

Sample	Engler viscosity		Specific gravity at 15°	Rise in U-tube		Pensky flash point	Burning point	Acid value	Saponifiable fat, per cent
	At 20°	At 50°		°C.	Mm.				
1	28 2	5 7	0 9177	−3 −5 Oil clear	19 0	164°	255°	2 24	26
2	49 0	7 6	0 9710	−15 −20 Oil clear	20 10	177°	252°	1 30	15

1. **Solubility of the Separated Fatty Acids in Petroleum Ether.** The fatty acids of unchanged oils, excepting those of castor oil which are easily characterized, dissolve entirely or almost so. Acids from blown oils because of their high content of oxy-acids (see table) give a precipitate, more or less large, depending upon the time and temperature of blowing.

2. **The Reichert-Meissl Value** shows the presence of the volatile acids formed in the blowing of the oils. See page 405. Certain fats (cocoanut oil, palm nut oil and butter fat, as well as several fish oils), which, however, are practically never found in lubricating oils, also have high Reichert-Meissl values.

3. In some instances it may be possible to draw conclusions regarding the presence of blown oil from the viscosity of the oil mixture and from the mineral oil separated from the material by the method of Spitz and Hönig. The unblown fatty oils with the exception of castor oil have an Engler viscosity of at most 15 at 20° (cottonseed, 9 to 10, rape, 11 to 15, generally near 13). If the viscosity of a mix-

ture is 30, that of the separated mineral oil 20, the increase in the value by 10 points cannot be caused by normal oil, but must be due to blown oil; this assumes the absence of thickening materials such as soaps, gelatine, etc.

4. The amount of blown oil in a mixture is determined indirectly according to Spitz and Hönig. A calculation from the saponification value is not always possible since these constants have too great a range.

114

Two Marine Oils

Mineral oil, per cent	Properties of the separated fatty acids				Lead salts of fatty acids soluble in naphtha	Composition
	Iodine value	Molecular weight	Reichert-Meissl value	Per cent of oxy-acids insoluble in petroleum ether		
74	80 7	272 7	8 05	15 3	Completely soluble in ethyl ether	About ¾ brownish-yellow, heavy mineral machine oil and ¼ blown rape oil.
85	75 9	272 4	5 04	15 6	The same	About 85 per cent brownish-yellow heavy mineral machine oil and 15 per cent blown rape oil.

In Table 114 are given the properties of two mixtures of mineral oil with blown rape oil.

5. The method of Sherman and Falk* to determine the original iodine value of the oil blown has been tested by Marcusson in the case of mixtures of mineral oils and blown oils (marine oils). For every increase of 0.001 at 15.5° in the specific gravity as referred to the original oil a positive correction of 0.8 in the iodine value is made; if the original specific gravity is not known, the average value for that kind of oil is used.

From the iodine value of the water-insoluble acids separated from the mixture (of which the blown oils contain about 90 per cent), the iodine value of the blown oils is calculated by multiplying by $\frac{9}{10}$. The unknown specific gravity x of the blown oil in the mixture can be calculated from the specific gravity (a) of the mixture and from that of the separated mineral oil (b) as well as the per cent of mineral oil (c) and per cent of fatty oil (d) as follows:

$$\frac{100}{a} = \frac{c}{b} + \frac{d}{x}$$

* Jour. Amer. Chem. Soc., May, 1905.

$$x = \frac{(a)(b)(d)}{(100)(b)-(a)(c)}$$

As the average specific gravity of the oil from which the blown material is obtained is taken 0.919 (rape at 15° 0.913 to 0.917; cottonseed 0.922 to 0.925). From the calculated specific gravity and the determined iodine value i of the sample of blown oil, the iodine value of the original oil J is found as follows:

$$J = i + \left[\frac{(S - 0.919)}{0.001}\right](0.8).$$

Marcusson found that the iodine values thus calculated were 8 to 10 units under the lowest values of rape oil (96); since furthermore the lowest for cottonseed (102) and the highest for rape oil (105) were so close together, it would appear that the method can be used only as a confirmation of the lead soap method, or to determine whether other oils are present.

O. Degras and Moëllon

I. General

In currying leather the material used for this purpose depends on the kind of leather and the use to which it is put. Industrially train oil and degras (an emulsion of oxidized train oil with water, tallow and soda) have been found indispensable. The train oil contains unsaturated acids which seem to have a tanning action (oil tannage) on the leather, a product being formed which has very desirable properties. The process may be carried out by hand or by means of machinery. In the latter method, the hides are treated with hot air in a rotating drum, the moisture being expelled and the oil sucked into the pores. This method is more advantageous than the hand process, as by it more solid materials, such as stearic acid, ceresine, paraffin can be worked into the leather.

Besides such currying compounds various preparations are offered for the preservation of leather articles such as harness oils, shoe creams and polishes. These may contain a great variety of fatty and greasy materials which increase the pliability and prevent the cracking of leather.

Under the terms degras* and moëllon are understood the fats used in currying bark-tanned and chrome-tanned leather. Degras, formerly obtained as a waste fish-oil product in the process of making chamois leather, has recently been made in special factories. Hides from which the hair has been removed and which have been made to swell by an acid fermentation are drenched with oil (whale, cod-liver

* The term degras is much used in the United States to cover the recovered wool grease obtained in the scouring of wool.

or menhaden), worked in a fulling machine for three hours and then exposed to the air for the same length of time. This operation is repeated until the skin is saturated with oil and the water driven out. The fish oil oxidizes somewhat under the influence of the air; to bring about more complete change, a further fermentation is allowed to take place. If the oxidation process goes on for some time (German and English methods), no more oil can be pressed out of the skins. To obtain the degras, the skins are washed with alkaline solutions; from the emulsion thus obtained, the fat is separated by means of sulphuric acid, the product always containing considerable amounts of water, soap and impurities, such as fragments of skin, etc. By the French method the skins are not fulled, aired or allowed to ferment so long as in the method described. Consequently by dipping the skin into lukewarm water, considerable amounts of oil can be pressed out. The moëllon thus obtained contains little ash or fragments and less water than the above.

Both kinds of material form homogeneous emulsions with oil and water; the emulsifying body, the so-called degras-former, a resinous, brown acid, insoluble in petroleum ether, soluble in alcohol and ethyl ether, is, as Fahrion has shown, a mixture of oxidized acids and their anhydrides. The melting point of these acids is, according to Jean, 65 to 67°.

The changes which the fish oils undergo in the formation of degras consist in an increase of the specific gravity from between 0.916 and 0.938 to between 0.921 and 0.984; the amount of the degras-former, that is the amount of petroleum ether-insoluble oxy-acids, becomes greater (the original fish oils contain 0.9 to 3.4, the oxidized oils 1.7 to 19.4 per cent); a rise of the acid value up to 28 takes place; and a lowering of the iodine value results. Qualitatively these changes correspond to the changes which blown oils undergo; therefore degras is made artificially by blowing air into heated fish oils.

Moëllon and degras easily penetrate in considerable amounts into the still moist skins, they bring about a uniform distribution of the fatty materials in the pores, they help to prolong the life of the leather, and prevent its drying out and spewing, and keep spots and mould from forming.

II. Examination

1. **Degras.** A commercial degras should, according to Wallenstein, contain more than 5 per cent of degras-former and less than 20 per cent water, a good moëllon, more than 10 per cent of degras-former and not more than 20 per cent water. In the examination it

is to be remembered, as Proctor pointed out, that moëllon is almost never sold pure but always mixed with tallow and untreated oil; these additions, if present in small amount, can hardly be considered as adulterations. On the other hand there are found on the market many more or less skillfully prepared mixtures (artificial degras) of untreated fish oil, of fish oil oxidized at higher temperatures by air, tallow, rosin, oleic acid, wool fat, mineral oil, etc.

(*a*) **Water.** Determined according to page 72. In heating to 110° oxidation and volatilization, with consequent considerable errors, may result. The amount of water in the sod oil may range from 20 to 40; in the moëllon from 15 to 25 per cent; Allen* states that "artificial" degras has a water content of from 10 to 12 per cent.

(*b*) **Fat Content** is determined by exhaustive extraction of the sample with petroleum ether, filtration and drying of the solution thus obtained, evaporation of the solvent, drying and weighing of the residue.

(*c*) **The Residue Obtained in** (*b*) **is Tested for Unsaponifiable Matter** according to page 76. Suspicion as to the presence of foreign unsaponifiable matter is aroused if more than 2 per cent is found; the nature of this material is determined by the methods of page 198 and following.

(*d*) **Resinous Substances (Degras-formers)** are determined by the method on page 413 (due to Fahrion). Besides having a low melting point, they can be distinguished from colophony by their insolubility in petroleum ether and by not giving the Morawski reaction.

(*e*) **Foreign Bodies,** *such as wool fat, oleic acid, tallow,* may be present if the specific gravity of the fat obtained according to (*b*) is less than 0.92, since the fat obtained from "natural" degras has the density 0.945 to 0.955. Furthermore in the presence of larger amounts of tallow, the melting point of the fatty acids is raised (fatty acids from tallow melt above 40°, acids from degras between 18° and 30°). Wool fat is detected by means of the higher alcohols (see page 519); colophony is detected according to page 182.

(*f*) **Ash** is determined by burning with a wick of filter-paper (page 73). Moëllon contains several hundredths of a per cent, degras as high as 3 per cent, of ash. Samples containing iron oxide give a grey color to the leather, consequently iron should always be tested for; and a sample should, according to Maschke and Wallenstein, not contain more than 0.05 per cent of iron.

2. **Other Leather Preservatives.** Many different materials are used to keep leather in good condition. Train oil, mineral oil, tallow,

* Chem. Rev., 13, 25 (1906).

stearic acid, ceresine, and paraffin in mixture with mineral oils are used; montan wax mixed with turpentine has been used as a shoe-cream.

The analysis of such materials follows the general schemes already described for other materials. At times complicated mixtures are compounded by foremen of tanneries or by leather workers. For the currying of leather and for softening and preserving finished leather various mixtures such as described in the following are found:

The ether insoluble residue (0.21 per cent) was soot-like, black, combustible, insoluble in alcohol, acids, and alkalies; it was soot, added to color the mixture.

The extracted fatty material was not very soluble in petroleum ether. On cooling a thick, yellow oil separated; this was soluble in 90 per cent alcohol, had a saponification value of 191, and seemed to be castor oil. The components, soluble with difficulty, seemed to indicate vaseline.

The soot-free material could be separated by hot alcohol into a white, high-melting body and a softer fat. The saponifiable component of the fat (48.2 per cent) was yellow and resembled vaseline. Alcohol extracted from it a small amount of oily, brownish-yellow material, which with concentrated alkali gave a violet red color (nitro-naphthalene reaction). Cholesterin seemed absent. The odor of the fat suggested an animal origin. The castor oil from 5 grams of the compound extracted with ether was then leeched with about 30 c.c. of 90 per cent alcohol, whereby about $\frac{1}{4}$ to $\frac{1}{5}$ of the total compound was dissolved. The alcohol-insoluble residue was boiled with $\frac{N}{2}$ KOH. The acids separated from the soap thus made melted at 38° and had the odor of bone oil.

In the original material and in the alcoholic extract the presence of nitro-naphthalene was shown by transformation into naphthylamine, and its behavior with ferric chloride (page 75).

Conclusion: The compound consisted of a mixture of unsaponifiable, vaseline-like material and saponifiable oil (castor oil and bone oil rich in solid glycerides). Nitro-naphthalene was present as a de-blooming agent. Soot was present to give a dark color to the mixture. Less valuable materials such as rosin, rosin oil, water, solid bodies, and mineral acids were not present. Only 1.83 per cent of free acid (calculated as oleic acid) was found; this amount corresponds to the amount normally occurring in the natural fats.

The most useful test of such leather preservatives is the practical trial with actual leather. It is important in treating calf skins that the hair side be uniformly covered with the oily material which should penetrate completely to the other side and not simply stay on the exterior surface.

P. Linoleum

Linoleum is an elastic material pressed on jute fibre; in Germany it is prepared by mixing highly oxidized linseed oil with cork, pine resin, kauri copal and similar bodies.

In the process of Walton, linseed oil is heated in large kettles with dryers (lead or manganese borates) and then allowed to drip in large chambers over vertically hanging cotton cloths. The varnish gradually solidifies by oxidation and polymerization to a jelly-like mass (linoxyn) with an evolution of penetrating fumes (of formic and acetic acids?). After several weeks the approximately 1.5 centimeter layer is melted together with rosin and kauri copal to a dark colored Walton cement, which is then cut up, dusted with chalk or powdered talc, and then melted up with ground cork and the coloring material (for the especial pattern desired) to form the actual linoleum. The cotton cloth becomes friable during the process and is ground up with the linoleum to a uniform, finely divided mass which is pressed between heated rollers into strips which in turn are pressed into blocks from which slabs are cut. These are then pressed by means of a liquid glue upon the jute or canvas cloth. The setting of the linoleum cement may require from 4 to 8 weeks.

The Taylor process requires much less time; it is used for the preparation of less-valuable linoleums. The crude material is obtained by heating linseed oil with dryers (lead oxides, etc.,) in the presence of air; it is cut up into small pieces, sprinkled with chalk or powdered talc, and then heated with ground cork and coloring material (ochre) in large kettles. The material is kneaded to uniformity and then pressed on jute, the strips of which are subjected for from 7 to 14 days to the action of steam at 45° in a special chamber to cause the setting of the linoxyn. The setting takes place suddenly and is recognized by the resistance of the material to scratching with a finger nail. The linoleum strips are used either with the same color throughout or a pattern in colors may be printed on it.

An inlay linoleum is made from a Walton cement; the separate colored blocks of different colors and design are pressed together, thus the colors run through the thickness of the linoleum.

Chemical Examination

The ash shows the presence of considerable amounts of inorganic filling material; incompletely oxidized linseed oil or the presence of foreign oils is shown by finding how much material is soluble in ether, in chloroform and in carbon disulphide, in which sufficiently oxidized linseed oil is almost completely insoluble. By treatment with boiling alcoholic alkali, linoxyn can be changed into soluble potassium salts of oxidized fatty acids. To test its wearing qualities the action of

water, dilute acids, alkali, soap, oils, petroleum and turpentine on the material is tried.

Mechanical Testin

More important than the little developed chemical examination is the more practical testing of the material as to its extensibility, its ability to be bent and its permeability to water. Normal* values for determining the value of a linoleum are not yet established.

Q. Iodized Fats

Iodized fats are prepared, according to patented processes, by the firm of E. Merck, Darmstadt, and the Aktiengesellschaft für Anilinfabrikation, Berlin, by treating semi-drying oils with an amount of iodine chloride or hydriodic acid insufficient for complete saturation. They are to be used as substitutes for cod-liver oils, the therapeutic value of which is ascribed to their small iodine content, and are said to help in cases of asthma, arterio-sclerosis, scrofula, etc. Sajodin, prepared by E. Fischer, is the calcium salt of iod-behenic acid and is one of the most used of these preparations. The testing of these materials must of necessity be largely a physiological one; the chemical tests are restricted to the determination of the amount of iodine and the ease of splitting off iodine. The value is supposed to increase with the amount of iodine contained and its ability to be absorbed and then be split in the body. The determination of chlorine in the presence of iodine is carried out as in the regular qualitative procedures.

R. Rubber Substitutes

I. Preparation and Properties

By the term " faktis " is meant a rubber substitute prepared from fatty oils (particularly, linseed, wood, rape, cottonseed and castor oils), either by heating with sulphur (brown faktis) or by the action of sulphur monochloride (white faktis). White faktis is a faint yellow, crumbly elastic mass of somewhat oily odor; it is soluble in ether with difficulty. Brown faktis is dark brown, like rubber, but more easily disintegrated.

The formation of these rubber substitutes takes place with the

* Burchartz, 17, 285 (1899)

addition of either sulphur monochloride or sulphur; the constitution of these bodies has been pictured as follows:*

$$\left.\begin{array}{l} X - CH - CHCl - y \\ \qquad | \\ \qquad S_2 \\ \qquad | \\ X - CH - CHCl - y \end{array}\right\}\text{White Faktis}$$

$$\left.\begin{array}{l} X - CH - CH - y \\ \qquad |\qquad\ \ | \\ \qquad S \qquad\ S \\ \qquad |\qquad\ \ | \\ X - CH - CH - y \end{array}\right\}\text{Brown Faktis}$$

According to Ditmar† linseed oil requires 30 to 35 per cent of S_2Cl_2, castor oil about 20 per cent, while cotton-seed oil needs 45 per cent. In the case of both brown and white "faktis" not only does addition of sulphur take place, but substitution probably also occurs. Furthermore a part of the free sulphur remains in the colloidal form.

TABLE 115

PROPERTIES OF WHITE AND BROWN FAKTIS*

	White faktis	Brown faktis
Sulphur, per cent	6.3 to 6.9	3 2 to 12.7
Chlorine, per cent	5.0 to 7 6	0 03 to 0.22
Ash, per cent	1.6 to 5 2	0 05 to 0 2
Saponification value	230 to 273	110 to 193
Acid value	0 6 to 2.7	0.3 to 1.5
Bromine value	24 to 38	98.5 to 130
Iodine value (calculated from bromine value)	37.7 to 59.7	154.6 to 204.1
Iodine value (direct by Wijs method)	16 to 31	13 to 51

* Vaubel, Gummiztg., **27**, 1254 (1912).

Both products are completely saponifiable with a formation of sulphurized fatty acids; in the saponification, the chlorine is split off from the white faktis as hydrogen chloride with the formation of another double bond.

II. EXAMINATION

Many of the rubber substitutes found on the market contain, besides sulphur or chlorine addition-products, some inorganic components, mineral oils and most of them also unsulphurized fatty oils; a

* Henriques, Z. angewandte Chem., **8**, 691 (1895).

† Seifenfabrikant, 1914.

good preparation should contain,* at most 3 per cent of ash, not more than 1 per cent of free sulphur and no large amounts of mineral oil. The external appearance should not be greasy. The examination is like that of rubber.† Allen states that good rubber substitutes sometimes contain paraffin besides mineral oil.

By extraction with acetone in a Soxhlet, the amount of free sulphur, fatty oil and mineral oil can be determined; the faktis is insoluble in acetone. In the extract, the fatty oil and mineral oil are quantitatively determined according to page 197; the amount of sulphur can be determined in the extract (and in the part insoluble in acetone) according to pages 77 and 78; chlorine according to page 79. Ash is determined by cautious ignition.

S. Soluble Castor Oil

By the patented process of Hugo Nördlinger of Flörsheim there is now prepared a castor oil soluble in mineral lubricating oil; this is also known as " derizinöl " and is obtained as a residue in the distillation of castor oil. It is used for thickening mineral lubricating oils. The distillate contains oenanthol, undecylic acid, acrolein, etc. Various products are available: a crude derizinöl, a product almost free from acid, and a medicinal oil for injections as in tuberculosis, and for mixture with ethereal oils.

T. Voltol Oils

Under the name of "Voltolöl " is sold a thickened product produced by the procedure of Hemptinne of Ghent from train oil; a silent electric discharge is allowed to act on the oil, a product being obtained which is very viscous and which possesses great lubricating power. It can be mixed with mineral oils.

U. Black (Recovered) Oil

This material‡ is prepared from the waste grease of woolen mills found under the carding and scribbling machines, being pressed or extracted with solvents. This oil contains, besides the oil used to oil the wool, some mineral oil from that used for lubrication. The latter is determined according to page 197.

* Lunge-Berl, **1911**, Bd. III, 847.
† Hinrichsen, Materialprüfungswesen, 506.
‡ Lewkowitsch, **2**, 730.

Other industrial recovered oils are met with; these are generally mixtures of mineral and fatty oils.

In the case of the adsorbent earths used for bleaching oils (such as margarines) it is possible to recover a fatty residue. Such fat is examined by the procedures already described.

CHAPTER VIII

WAXES

I. Composition

The true fats and oils are glyceryl esters, while waxes contain no glycerine. The waxes are esters of high molecular fatty acids with alcohols, in part aliphatic, in part, aromatic; in them are found, however, free fatty acids, free alcohols and hydrocarbons; for example, beeswax contains considerable free cerotic acid, $C_{26}H_{52}O_2$, the main component myricyl palmitate, $C_{16}H_{31}O_2 \cdot C_{31}H_{63}$, besides high melting hydrocarbons. Chinese wax contains mainly ceryl cerotate, $C_{26}H_{51}O \cdot C_{26}H_{53}$.

The acids occurring in waxes appear to have an even number of carbon atoms.* Spermaceti is mainly cetyl palmitate, $C_{16}H_{31}O_2 \cdot C_{16}H_{33}$. With the exception of the liquid waxes (sperm oil and bottlenose oil) all waxes, on boiling with alcoholic potash and subsequent treatment with water, give a cloudiness or a precipitate, since the higher alcohols are only slightly soluble in the resulting aqueous soap solution.

On heating the waxes, since they are not glycerides, no acrolein odor will develop (see, however, sperm oil). The saponification values of all waxes are decidedly lower than those of the glycerides because of the large amount of unsaponifiable alcohols contained (see Tables 116, 117 and 118). With fats 15 minutes heating is sufficient, with waxes at least an hour is required for saponification (regarding the use of xylol as a solvent for saponification, see pages 520 and 524).

II. Special Properties of Liquid Waxes

The odor, taste and several color reactions of liquid waxes are much like those of blubber; their origin being similar, the former are sometimes mistaken for the latter. To distinguish between the two, the large amount of unsaponifiable matter in the waxes (35 to 40 per cent) as well as the low specific gravity (0.875 to 0.883 for waxes as against 0.915 to 0.937 for train oil) will serve to characterize the waxes.

The solid waxes with the exception of wool fat consist principally of saturated compounds; the liquid waxes, however, are compounds of unsaturated alcohols of the $C_nH_{2n}O$ series with unsaturated fatty

* Henriques, Ztschr. f. angew. Chem., **11**, 368 (1898).

TABLE

CONSTANTS OF THE

	Specific gravity, 15°	Solidification point, °C.	Saponification value	Iodine value		Reichert-Meissl value
				Of the oil	Of the fatty acids	
Sperm oil, Spermazetiöl, Pottwaltran, Huile de spermaceti	0 8799 to 0 8835	Not much under 0°	120 to 137 (150)	81 to 87 (90)	83 to 88	1.3
Arctic sperm oil, Bottlenose oil, Doglingtran	0 8764 to 0 8808	....	126 to 130 (136)	67.1 to 84.5	80 to 82	1 4

acids. Recently, there has been found* in sperm oil glycerine (see Table 116). The two liquid waxes, sperm oil and arctic sperm oil, are hard to distinguish chemically; industrially the arctic sperm oil is easily recognized by its characteristic taste. Sperm oil is a valuable lubricant for spindles and light machinery, since it does not easily become rancid, does not resinify on the bearings and its viscosity decreases only slowly with a rise in temperature; arctic sperm oil resinifies more easily and is therefore not valued so highly.

* Fendler, Chem. Ztg., **29,** 555 (1905); Dunlop, J. soc. Chem. Ind., **1908,** 63.

116

LIQUID WAXES

Hehner value	Melting point of the fatty acids	Solidification point of the fatty acids	Main components	Other properties
60 to 64	13 3 to 21 4	16 1, Titer test 11 1 to 11.9	Esters of fatty acids (60 to 64 per cent), oleic (?) series, and 36 to 41 5 per cent high molecular monatomic alcohols provided that oil was not pressed too much.	Faint odor of blubber. Engler viscosity 5.6 to 7.05 at 20°. Melting point of the higher alcohols 25.5 to 27.5 (Lewkowitsch), 32.5 (Fendler) Iodine value 64.6 to 65.8. The higher alcohols are insoluble in water, soluble in alcohol. Glycerine* 1.32 to 2.51 per cent.
61.7	10.3 to 10.8 (16 1)	10 1, Titer test 8 3 to 8 8	Esters of fatty acids (oleic acid series) and 32 to 43 per cent of monatomic alcohols of high molecular weight.	Has faint blubber odor, tendency to become resinous. Melting point of the higher alcohols 23.5 to 26 5°. Iodine value 64.8 to 65.2. The higher alcohols act towards solvents as do those of sperm oil.

Detection of Additions. The comparatively high price of sperm oil leads to adulterations with fatty oils and mineral oils. The former are detected by the increase in specific gravity and saponification value; the latter qualitatively by the saponification test of page 76, quantitatively according to page 197 by treatment of the unsaponifiable matter with acetic anhydride. An addition of arctic sperm oil to sperm oil can probably not be detected.

III. Properties of Solid Vegetable Waxes

TABLE 117

	Specific gravity, 15°	Solidification point, °C.	Saponification value	Iodine value of the wax	Main components	Other properties
Carnauba Wax. *Carnauba-wachs, Cire de carnaube*	0 990 to 0 999	Fresh 80 to 81, old 86 to 87, melts according to age from 83 to 91	79 to 86 5	10 1 to 13 5	Myricyl alcohol, myricyl cerotate, little cerotic acid, 55 per cent unsaponifiable	Green crude, white when purified; give characteristic odor on burning Saponified with difficulty by alcoholic potash.
Flax wax, *Flachswachs, Cire de lin*	0 907	. ...	102	9 6	Stearic, palmitic, oleic, linoleic, linolenic, isolinolenic acids, ceryl alcohol, phytosterin, 55 to 65 per cent hydrocarbons and an aldehydic body in 81 per cent unsaponifiable material.	. ...
Candelilla wax*	0 936 0 950 to 0.993	63.8 to 68, melting point 67 to 70	47 to 65	12 to 20 57 6 Wijs	65 to 77 (91.2) per cent unsaponifiable, 29.4 per cent (6.6) fatty acids; 0.34 per cent ash; 18 to 20 per cent resinous material, 74 to 76 per cent of $C_{32}H_{66}$ or $C_{30}H_{62}$ and 5 to 6 per cent oxy-lactone $C_{30}H_{56}O_2$.	Acid value 12 to 21; ester value, 32 to 82; N_{70} = 1.4558. Obtained in Mexico from Pedilanthus Pavanis, substitute for carnauba wax

* Harre and Bjerregaard, Zeit. f. angew. Chem., **1910,** 471. Neiderstadt, Seifensiederztg., **1911,** 1145. McConnel-Sanders, Chem. Ztg., **35,** 1346 (1911), Meyer Monatshefte, **34,** 531 (1913) Berg, Chem. Ztg., **38,** 1162 (1914).

IV. Properties of Solid Animal Waxes

TABLE 118

	Specific gravity, 15°	Solidification point, °C.	Saponification value	Iodine value of the wax	Main components	Other properties
Cetin, *Spermaceti*, *Walrat*	0 945 to 0 960 895†	42 to 47 melts 42 to 45 (49)	123 to 135	3 8	Cetyl palmitate and small amounts of the glycerides of lauric, myristic, and palmitic acids, 53.45 per cent fatty acids	Easily soluble in hot alcohol. Easily saponified by alcoholic potash. Crystalline structure.
Wool fat, *Wollfett*, *Suint*	0 941 to 0 970	Fatty acids 40, they melt between 31 and 42	82 to 130	15 to 29, iodine value of the fatty acids 17	Iodine value of the unsaponifiable 26.4 to 36, melting point 33.5. See page 519	See page 519
Beeswax, *Bienenwax*, *Cire des abeilles*	0 958 to 0 967 (0 975)	Melts between 63 to 64 (70)	91 to 98	8 to 11	Mixture of cerotic acid, myricyl palmitate and solid hydrocarbons	Acid value 19 to 21, ester value 72 to 76 (81), ratio (Hübl) 3 6 to 3.8. 52 to 55 per cent of higher alcohols and hydrocarbons. Hydrocarbons have iodine value 22.*
Insect wax, Chinese wax, *Insektenwachs*, *Chinesisches wachs*, *Cire d'insectes*	0 926 to 0 970	80 5 to 81 0 melting point 80 to 83	78 to 93	1 4	Ceryl cerotate and other esters. 51 5 per cent fatty acid	Little soluble in alcohol, ether and petroleum ether. Yellow white in color and crystalline structure.

* According to Ahrens and Hett, 12.7 to 17.5 per cent. The melting point of the total unsaponifiable matter is 72 to 78°, after acetylation, 52° to 64°; completely soluble in hot acetic anhydride but almost completely insoluble cold. Paraffin and ceresine do not have a changed melting point after acetylation.

† Lucas, Apoteker Ztg., **28**, 570 (1913).

V. Wool Fat* (Wool Grease)

(*a*) **General.** Wool fat is obtained by extraction of raw wool with volatile solvents, such as naphtha, benzol, carbon disulphide, or by scouring the wool with soap solutions, or with dilute ammonium or sodium carbonate solutions, these solutions being then acidified with sulphuric acid. The method of extracting by means of solvents has not been entirely satisfactory; the wool is either attacked by the solvent or de-greased too much. The method has been improved by using inert gases during the extraction, and the evaporation of the solvent. The de-greasing is brought about generally by means of dilute soap solutions, the wash waters containing from 1.5 to 2 per cent of fat. The emulsion is broken up in cement tanks by sulphuric acid, the acid being used again. The settled grease is pressed in cloth and brought on the market as crude wool fat.

In the crude state, the fat is a greasy, ill smelling, yellow or brown mass. After removal of the free acids and the soaps from the raw fat by various (patented) processes, the refined wool fat, sometimes called lanolin, is obtained. It is white or pale yellow, translucent, of salve-like consistency and almost odorless; it takes on over 300 per cent water with the formation of permanent emulsions. The affinity for water is not due to the esters of the wool fat but is caused by the presence of cholesterins, especially an oxy-cholesterin, recognized by the glacial acetic-sulphuric acid reaction. These alcohols (cholesterins) mixed with vaseline produce a salve like material which has found use in medicinal applications.

(*b*) **Composition.** Wool fat is a complicated mixture of esters and alcohols of high molecular weight. Fatty acids (palmitic, cerotic, oleic, stearic and volatile acids) were found†, also myristic, carnaubic, lanoceric ($C_{30}H_{60}O_4$) and lanopalmic ($C_{16}H_{32}O_3$) are said to be present‡. Lactones of some oxyacids are also supposed to be present, as well as an oily fatty acid which is not oleic acid.

The alcohols make up as much as 55 per cent of the wool fat, and are a mixture of ceryl alcohol ($C_{27}H_{56}O$), carnaubyl alcohol ($C_{24}H_{50}O$) cholesterin (small amount) and iso-cholesterin (up to 20 per cent).

* With the assistance of J. Lifschütz. Berichte **31,** 1122 (1898); **29,** 618, 1474, 2890 (1896); **30,** 2898 (1897). D.R.P. 167, 849.

† Sanctis, Gazz. chim. ital., **24,** 14 (1894).

‡ Darmstädter and Lifschütz, Ber., **20,** 618, 1474, 2890 (1896); **30,** 2898 (1897); Zeit. physiolog. Chem., **56,** 451 (1908). Schulze, Ber., **12,** 149 (1879). Biochem. Zeitsch., **54,** 233 (1913).

Oxycholesterin and oxidation products of oleic acid probably are also present. "Lanolin alcohol" is the lactone of lanoceric acid. The purified wool-fat contains 3 to 4 per cent of free cholesterin and 16 to 18 per cent of cholesterin derivatives.

(*c*) **Examination.** The color reactions 1 and 2 for recognition of wool fat are given by the cholesterin present.

1. **Liebermann Reaction.** One quarter gram of fat is mixed with 3 c.c. of acetic anhydride, filtered, and the filtrate treated with 1 drop of concentrated sulphuric acid; a red to brown color develops, which rapidly changes to dark green. This reaction must not be confused with that given by rosin and rosin oils (pages 186 and 200); with these substances the red-violet color changes into an uncertain brown. The isocholesterin of wool fat influences this reaction.

2. **Hagar-Salkowski Reaction.** One quarter of a gram of wool fat in 10 c.c. of chloroform is shaken with 10 c.c. of concentrated sulphuric acid. The acid assumes a blood red color and shows a strong green fluorescence. The color persists for days.

3. One gram of wool fat is boiled with 2 to 3 c.c. of glacial acetic acid, filtered, the filtrate mixed with 1 c.c. of chloroform and then 8 drops of concentrated sulphuric acid added. A yellow-red color develops, then blue-green and finally green. This is characteristic of oxycholesterin, which is not given by cholesterins. In the presence of a drop of ferric chloride, the color will appear in a few seconds.

4. Pure cholesterin treated as in (1) does not give the color change, red-blue green but gives first a greenish-yellow, then a blood-red with green-yellow fluorescence. In the spectroscope a dark band is seen in the green towards the yellow, in great dilution a band in the blue. Cholesterin does not influence the sensitiveness of this reaction. The reaction develops in 20 to 30 minutes and persists for many hours. The reaction is more characteristic of wool fat than the others just mentioned as cholesterin occurs in many fats.

5. **Water** to be determined as on page 71.

6. **Acid Value** is to be determined according to page 69 with about 4 grams of fat.

7. **Saponification Value.** Wool fat contains small amounts of esters* which are split only under the influence of N/2 alkali and under pressure at 105°, the main portion being changed under normal pressure. The saponification value is determined by three hours boiling on a water bath with N/2 alkali; the titration should be made hot, for otherwise difficultly soluble potassium salts may separate and influence the sharpness of the end-point.

8. **The Iodine Value** is to be determined according to page 406 with a 0.5 gram sample.

9. **Unsaponifiable Alcohols.** These higher alcohols cannot be separated from the fatty acids by the method of Spitz and Hönig, for wool-fat soaps are decidedly soluble in naphtha.

* Herbig. Din. Poly. Jour., **292**, 42–66.

2 grams of wool fat with 25 c.c. of N/2 alcoholic potash are heated for 3 hours in a water-bath at 105° (brine bath), the solution washed with alcohol into an evaporating dish, neutralized (phenolphthalein) and then heated to boiling, after driving off the alcohol with 50 c.c. of water. If a cloudiness develops, a small amount of alcohol is added. A 10 per cent excess (calculated from the saponification value) of calcium chloride solution is then added at 70° to 75° in a thin stream and with constant stirring to the soap solution; after diluting with two volumes of water, adding also a few c.c. of alcoholic potash, the calcium salts separating cold are filtered off with suction and washed with cold alcohol (1 : 20) till the filtrate is free from chlorides. The filter with contents is dried at least 48 hours in a vacuum desiccator to remove water completely, then extracted in a Soxhlet with freshly distilled acetone; the extract is dried 1 hour at 105° and weighed. The extract should be neutral and ash free.

Simpler is the following: 4 grams of wool fat are boiled with 50 to 60 c.c. of alcoholic N/2 KOH for 3 hours. The excess alkali is neturalized with hydrochloric acid, the solution evaporated to dryness. The residue is mixed with Na_2SO_4, extracted in a Soxhlet with ether (freshly distilled over sodium) and the extract washed with 20 per cent alcohol. After evaporation of the ether, the residue of unsaponifiable matter is dried and weighed.

The substances thus obtained are to be characterized as alcohols by solution in two volumes of hot acetic anhydride (on cooling, the solution will be at first clear, but on longer standing crystalline, non-oily material will separate), by their complete solubility in two volumes of slightly warmed absolute alcohol, by iodine value (about 30), by melting point (about 33), by color reactions (1 and 2) and perhaps by determining the acetyl value.

Very characteristic of the wool fat alcohols is the insolubility of isocholesterin in methyl alcohol. The melted mass of the unsaponifiable matter is covered with methyl alcohol and heated to 60° C. The isocholesterin remains as a white powder; this can be dissolved in ethyl alcohol and be reprecipitated by methyl alcohol and thus purified. Very small amounts of isocholesterin can be thus identified.

10. **Foreign Unsaponifiables.** Paraffin, mineral oil and rosin oil are weighed with the higher alcohols (as under 9). They separate (after boiling with acetic anhydride and then cooling) as a layer on top of the anhydride. These bodies are determined quantitatively by repeated leaching with acetic anhydride, and weighing the undissolved material after washing out the acetic anhydride; of course not exactly, since even paraffin, mineral oil and rosin oil are soluble (mineral oil almost 8 per cent, hard paraffin almost not at all, soft paraffin only in traces)

11. **Foreign Saponifiable Fats** are recognized by their glycerine content, this being determined according to page 458 (method of Benedikt and Zsigmondi). Any acetone present from the process would also be oxidized to oxalic acid and should be removed by previous steam distillation; or another method may be used (Shukoff).

12. **Rosin.** Rosin cannot be detected by the Morawski reaction, since the cholesterin present will itself give an intense color reaction with acetic anhydride and sulphuric acid. If, because of high acidity and the sticky nature of the extract prepared with 70 per cent alcohol, rosin is suspected, an ether solution of the fat is

extracted with $\frac{N}{10}$ soda, the extract acidified and the separated acids tested by the Morawski reaction.

13. **Additions** of fatty acids, since thev usually contain oleic acid, can be detected* as follows:

0.2 grams of fat in 4 c.c. of glacial acetic acid are boiled with chromic acid-acetic acid mixture till a green color appears, then 12 to 15 drops of H_2SO_4 are added and the mixture heated to 80°. The solution shows with the spectroscope a wide absorption band in the green near the blue, a smaller and fainter band near the yellow and a faint line between the orange and yellow. One part oleic acid in 15,000 can be detected. Wool fat and its oleins do not give this reaction.

(*d*) **Wool-fat Oleins.** 1. **General Properties.** Wool-fat oleins are obtained by distillation of the crude wool grease with superheated steam, then separating the solid components by cold pressing.

Wool-fat oleins are not suited for oiling wool before spinning; they are however used in preparing machinery greases.

They are yellow to red-brown, in part green, in part blue fluorescent oils with an odor like that of wool fat; specific gravity between 0.90 and 0.92. The characteristic reactions for cholesterin (Hagar-Salkowski and the Liebermann) are given by these materials. Isocholesterin, which does not give these reactions, may be tested for by the methods given under wool fat; these tests are said to be more conclusive than those for cholesterin since other fat-distillates may give the cholesterin tests.

Wool-fat oleins may contain from 40 to 60 per cent of fatty acids (including some caproic, butyric, myristic, and a considerable amount of an oily acid which gives the fatty character to the distillate), saturated and unsaturated hydrocarbons† (from 10 to 53 per cent), small amounts of unchanged esters, and uncombined, high-boiling alcohols.

2. **Analysis.** The value of the fat is decidedly affected by the unsaponifiable matter, since it is washed out of the wool only with difficulty and consequently gives rise to spots and streaks.

3 grams of the olein are heated 3 hours with 25 c.c. of 2 N KOH in a sealed tube at 105° (brine bath). The unsaponifiable is extracted‡ by the method of Spitz

* Z. physiol. Chem., **56,** 446 (1908).

† Gill and Forrest, J. Amer. Chem. Soc., **32,** 1071 (1910), Richards, J.A.C.S., **30,** 1282 (1908). Marcusson, Z. angew. Chem., **25,** 2577 (1912).

‡ When the unsaponifiable is being extracted from the crude wool fat, it is advisable to extract the potassium salts with acetone (page 197); with distillates, this is not necessary since after distillation there are no acids present which might give soaps soluble in naphtha.

and Hönig and the extract boiled for two hours under a reflux with acetic anhydride to separate the higher alcohols. The portion insoluble in acetic anhydride, after washing with hot water, has the appearance of light machinery oil, but may be distinguished from this by the following reactions of the unsaponifiable hydrocarbons of the wool-fat hydrocarbons:

They give the Hagar-Salkowski and the Liebermann reactions very sharply.

They have an optical rotatory power of $\alpha_D = +18°$ to $+28°$ (mineral oils not over 2.2°).

They absorb considerable iodine (Waller iodine value 50 to 80; mineral oils generally less than 6, rarely over 14).

A simple test* is given by the solubility in alcohol. 5 c.c. of olein are shaken with 5 c.c. of a mixture of ethyl and methyl (1 : 9) alcohols at 20°; in this way most of the oleins free from mineral oils dissolve clear or with only faint turbidity. If, however, 10 per cent of mineral oil is present, the solution becomes milky and after standing oily drops appear. If the solution remains clear, mineral oil is absent. By this test 20 per cent of rosin oil may also be detected.

The unsaponifiable matter separated by the method of Spitz and Hönig is further tested; in the absence of rosin oil, it has an index of refraction of 1.49 to 1.51 (like mineral oil); if rosin oil is present, the index is higher. Rosin oil also raises the specific gravity (0.97 to 0.98, olein 0.905 to 0.912).

Rosin which is sometimes added as an adulteration is detected qualitatively by the Morawski reaction; quantitatively according to page 186. In making the Morawski test, it is important that the unsaponifiable matter in the olein be first separated (since it gives the Liebermann reaction which is very similar to the Morawski one) and the test made with the acids obtained from the soap solution. These give no red-violet color with oleins free from rosin.

(*e*) **Salve-like Wool-fat Distillate** (Marcusson and Skopnik) results when the portion of the wool-fat distilling with steam between 300° and 310° crystallizes, the olein being then drained off. The product is white to pale yellow, with solidification point under 45°; it is used in making lubricating greases.

It contains 16 to 33 per cent of unsaponifiable matter, which is like that of wool-fat olein, but having a lower rotatory power ($[\alpha]_D = +12.5°$ to 20°) and a higher iodine value (60 to 74). It furthermore contains 40 to 60 per cent of solid acids of melting point 41 to 47°, of iodine value 10 to 15 and of molecular weight 258 to 267; it also contains 20 to 25 per cent of liquid fatty acids of the iodine value 43 to 48 and molecular weight 270 to 302.

The examination of the salve-like wool-fat distillates is made very much in the same manner as in the case of the oleins; it must be remembered that the rotatory power of the unsaponifiable part of unadulterated wool-fat distillates may go as low as $+12.5°$ and that the solid acids interfere with the methyl-ethyl alcohol solubility test.

* Winterfeld and Mecklenburg, Mitteilungen, **28**, 471 (1910).

(*f*) **Wool-Fat Stearine** is obtained with olein by subjecting the cooled products of steam distillation, which pass above 310°, to 200 atmospheres pressure; a dark yellow mass, melting over 45°, with the odor of wool fat is obtained. It is used in stuffing leather (belting), for the preparation of waterproof packages, etc. It is not used as a soap stock. It lacks crystalline structure and gives the Liebermann reaction. It contains 32 to 42 per cent of unsaponifiable materials (with an iodine value 47 to 56 and a rotatory power of + 24° to + 31°) besides 58 to 68 per cent of solid fatty acids (of melting point 60 to 67°, iodine value about 10 and the molecular weight 318 to 382).

VI. Analysis of Beeswax

(*a*) **General.** The crude material obtained by melting of the comb is generally yellow, sometimes grey or reddish brown, brittle, granular, tasteless and having the odor of honey. To prepare white wax, the crude wax is remelted with water, then bleached in sunlight after the addition of 3 to 5 per cent of tallow or small amounts of turpentine; the material is first either granulated or pulled into threads or ribbons. The additions according to C. Engler act as oxygen carriers. White wax is odorless, translucent at the edges and denser than yellow wax.

(*b*) **Examination.** Beeswax is often adulterated with powdered mineral matter as well as with tallow, stearic acid, Japan wax, carnauba wax, rosin, paraffin and ceresine. Before analysis, the sample must be leached free from honey by boiling with water and then filtering through a hot water funnel. Mineral adulterants remain on the paper.

Its specific gravity is 0.963 to 0.970 at 15°, 0.818 to 0.822 at 98 to 100°; melting point 63 to 64°. Of great importance is the determination of the ratio of the acid value to the ester value, which is constant within narrow limits (3.6 to 3.8 with yellow wax, 3.0 to 4.0 with white wax; see Table 118, page 517).

The following method is used to saponify* wax completely:

4 grams are boiled with 20 c.c. of xylol and 20 c.c. of absolute alcohol under a reflux condenser, using an asbestos gauze with small flame. The hot liquid is immediately titrated with $\frac{N}{2}$ alcoholic potash. After the acid value has been thus determined, 30 c.c. of $\frac{N}{2}$ alcoholic potash are added and the mixture kept vigorously boiling for 1 hour. Then 50 to 75 c.c. of 96 per cent neutralized alcohol are added, heated for 5 minutes and then rapidly titrated with $\frac{N}{2}$ hydrochloric

* Berg. Pharm. Zentralh., **1906**, 230; Bohrisch and Kürschner, ibid., **1910,** No. 25/26.

acid; after again boiling for 5 minutes, the solution is titrated to the final end-point. The acid and ester values and the ratio of these two quantities of the substances to be considered are given in Table 119.

TABLE 119

	Acid value	Ester value	Ratio
Beeswax	19 to 21	72 to 76	3.6 to 3.8
Carnauba wax	4 to 8	76	9.5 to 15.5
Paraffin, ceresine	0	0	0
Japan wax	20	195	9 75
Tallow	10	185	18.50
Rosin	130 to 164	16 to 36	0 13 to 0 26
Stearic acid	200	0	0

Hübl draws the following conclusions from the ratios:

1. If the ratio for a wax is between 3.6 and 3.8, and the saponification value is less than 72, paraffin or ceresine must be present.

2. If the ratio is greater than 3.8, Japan wax, carnauba wax or tallow may be present. With an acid value under 20, Japan wax is absent; with a ratio under 3.8, stearic acid or colophony are probably present.

With artificially bleached waxes the above values do not hold. East Indian beeswax also shows values diverging from these. Waxes from Tunis were frequently found in Germany before the war and these, though unadulterated, had the ratio 3.9 to 4.5*. It must furthermore be remembered that wax-like mixtures can be easily prepared, which, although free from beeswax, have the normal ratio. Such a mixture, for example, can be prepared by melting together 37.5 parts of Japan wax, 6.5 parts of stearic acid and 6.5 parts of paraffin or ceresine. In cases of doubt therefore the determination of the ratio is not sufficient; it must be checked by one or more of the methods discussed in the following pages.

Indian beeswax (Ghedda wax) seems to be distinct from that from apis mellifica; it appears to originate from apis dorsata, apis indica, and apis florea. In Table 120 are collected some of the values used by Indian chemists.†

Beeswax contains myricyl alcohol and little ceryl alcohol, East

* Chem. Ztg., Rep., **22**, 235 (1898).

† Z. öff. Chem., **3**, 570 (1897); **19**, 147, 170, 188, 354 (1913); **20**, 315, 409, 435 (1914); **21**, 53, 145 (1915). Chem. Ztg., **29**, 297 (1905); **30**, 30, 43 (1906); **31**, 537 (1907).

Indian wax contains only ceryl alcohol.* There are differences in the esters contained. Hydrocarbons ($C_{26}H_{54}$ and $C_{30}H_{62}$) occur in both. The ratio of hydrocarbons to alcohols is not the same for domestic and Indian beeswax.

TABLE 120

Wax from	Melting point	Acid value	Ester value	Saponification value	Iodine value Hübl	Ratio
India						
apis dorsata	60 to 67	4 4 to 10.2	69 5 to 97 8	75 6 to 105.0	4 8 to 9.9	.....
apis florea	63 to 68	6 1 to 8 9	80 8 to 123.8	88 5 to 130.5	6 6 to 11.4	... .
apis indica	62 to 64	5 0 to 8 8	84 0 to 95.9	90 0 to 102.5	5 3 to 9 2	. ...
Trigona (melipona)	66 to 76	16 1 to 22 9	55 2 to 128.3	73 7 to 150.0	30 2 to 49.6	. ...
Ghedda wax		5 3 to 12.2	75 2 to 103.1	81 8 to 110.4	.	7 4 to 18.8
China,						
Beeswax	.	5 3 to 9.7	76 1 to 111.5	82 1 to 120.2	. . ...	11 0 to 17.9

1. **Glycerides,** such as tallow, are determined by estimation of the glycerine, according to page 458.

2. **Stearic Acid** is detected by heating 3 grams of wax with 10 c.c. of 80 per cent alcohol, cooling with stirring, filtering the clarified extract and precipitating the dissolved material with water. Under these conditions stearic acid only will separate; the cerotic acid present in beeswax is precipitated completely when the alcoholic solution is cooled. It is said that by this test 1 per cent of stearic acid can be detected in a wax. Colophony, however, acts like stearic acid, but can be detected according to 5.

It is also possible to neutralize the alcoholic extract with alcoholic sodium hydroxide, extract the unsaponifiable from the 50 per cent alcoholic solution with naphtha, precipitate the stearic acid from the soap solution and then characterize the stearic acid by its molecular weight and its melting point. In this case, the commercial stearine may be supposed to have a molecular weight of 276 and a solidification point of 53 to 57°; crude cerotic acid has a molecular weight over 396, melting point 78 to 82°.

A faint stearic acid test does not indicate adulteration as the palmitic acid present in every wax acts similarly; the acid must therefore be separated and identified. The small amounts of liquid unsaturated acids present in wax, and the free acids formed in the bleaching of wax from esters present, may interfere with the above test.

3. **Carnauba Wax** increases the specific gravity of the wax and its melting point, insect wax, however, only the melting point (see Table 118).

4. **Paraffin and Ceresine.** (*a*) As little as 5 per cent of these bodies† may be found through the insolubility of unsaponifiable matter of pure waxes in glycerine.

* J. prakt. Chem., **86,** 184 (1912)

† Weinwurm, Chem. Ztg., **21,** 519 (1897).

By heating 5 grams of wax with 25 c.c. of N/2 alcoholic potash for one hour, evaporating the alcohol, warming the residue on a water bath with 20 c.c. of pure glycerine till dissolved and then adding 100 c.c. of boiling water, pure beeswax will give a more or less transparent or translucent solution through which ordinary type may be easily read; in the presence of 5 per cent paraffin or ceresine the solution is cloudy and the type no longer visible; with 8 per cent, a precipitate will be obtained. In the presence of carnauba wax or insect wax, a cloudiness will develop even in the absence of paraffin and ceresine; these waxes can be detected according to 3. The precipitates, forming on the addition of hot water to the saponified wax, may be due to paraffin, or to other causes, according to Buchner.* The spongy precipitate is remelted with water, dried, boiled two hours under a reflux condenser with acetic anhydride and allowed to cool. If a wax-like layer forms on the top of the clear liquid, only paraffin is present; if the entire mass has set to a network of crystals without a wax-like layer on top, then only alcohols are present; while if a wax-like layer is found on top of a mass of crystals, both alcohols and paraffin are present.

(*b*) Paraffin or ceresine may be approximately determined by changing the fatty alcohols into fatty acids† by heating with soda-lime. The hydrocarbons are not attacked by this method; beeswax is said to contain 12.7 to 7.5 per cent of hydrocarbons. The method is said to be inexact as part of the alcohol is unchanged and on extracting with ether mixes with the hydrocarbons. Melissyl alcohol on heating with soda-lime to 250° was only 96 per cent decomposed.

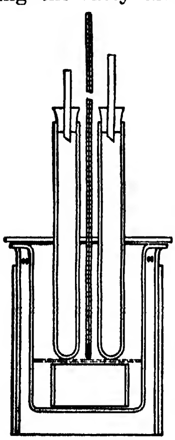


FIG. 136.

To 1 gram of wax, melted in a hard glass test tube (20 by 2 cm.), is added 3.5 to 4 grams of granulated potassium hydroxide, previously dehydrated in a silver dish (Fig. 136); the wax is immediately absorbed by the alkali. Two grams of potassalime are added and the tube is closed with a stopper carrying a glass tube for leading off any gas. The tube is then heated to 260° in a copper oven till no more gas bubbles will pass through the glass tube, the end of which is dipping below water (3 to 4 hours). When cool, 3 c.c. of water are added to the porous, fused mass and then after stoppering, it is heated for two hours to 100° in order to soften the material; the mixture is then transferred to a porcelain dish, the last portions being removed from the tube with dehydrated gypsum. The material is powdered, dried 1 to 2 hours, again powdered and then extracted with ether; this solution is dried, the solvent evaporated and the residue weighed.

(*c*) To separate the unsaponifiable hydrocarbons in beeswax from

* Ztschr. f. offentlich. Chem.

† Buisine, Ahrens and Hett, Ztschr. f. öffentl. Chem., **5**, 91 (1899). Ryan and Dillon, J. Chem. Soc., **110**, 706; Z. angewandte Chem., **30**, II, 181 (1917).

the alcohols, use is made of the insolubility of the hydrocarbons* in a mixture of fuming hydrochloric acid and amyl alcohol, in which myricyl alcohol is soluble.

Ten grams of wax are heated 20 minutes with 25 c.c. of alcoholic $\frac{N}{1}$ potash and 50 c.c. of benzol for tweny minutes under a reflux condenser, then 10 minutes after adding 50 c.c. of water; the lower alcoholic layer being then drawn off, the benzol solution is boiled 10 minutes with 50 c.c. of water, the lower layer being added to the main portion of soap solution. After the solvent has been evaporated from the benzol solution, the residue (with pure beeswax this is about 50 per cent) is dissolved in a tall beaker in 100 c.c. of amyl alcohol and 100 c.c. of fuming hydrochloric acid, heated to boiling with stirring and then allowed to cool slowly. On cooling, the wax alcohols separate in a crystalline condition, while the hydrocarbons are insoluble, even when the solution is hot, and collect on the top as a cake which can easily be lifted off. This cake (which is very thin with pure beeswax) can be treated in the same way as just described to remove the last traces of myricyl alcohol. The hydrocarbons and the alcohols can then be weighed separately.

To obtain the alcohols, the mass of crystals is transferred to a porcelain dish with hot water and benzol; the mixture is warmed till transparent. On cooling, the dilute HCl is decanted from the solidified solution of the wax alcohols in amyl alcohol. After evaporation of the amyl alcohol, the wax alcohols are washed into a weighed dish with benzol, the latter evaporated and the residue weighed.

This method has been found useful.†

(*d*) The constant acetyl value of beeswax alcohols (namely, 122) has been used by Buchner and Deckert‡ for the quantitative determination of paraffin additions.

The mixture of alcohols and hydrocarbons prepared as above under (c) is not separated with amyl alcohol and hydrochloric acid, but is washed with hot benzol into a 100 c.c. flask and boiled under a reflux condenser for 3 hours with 10 c.c. of acetic anhydride. The contents of the flask are washed into a porcelain dish with benzol and then heated to remove the acetic anhydride. The residue is rinsed into a flask (again with benzol) and saponified (as described for beeswax). From the acetyl value (*a*), assuming that of the beeswax alcohols to be 122, it is possible to calculate the amount contained, as follows: —

$$X : a : : 100 : 122$$

Buchner§ found 38.0 to 39.8 per cent of alcohols, and 11.7 to 11.9 per cent of hydrocarbons in normal beeswax; for two East Indian

* Leys, Jour. Pharm. et Phys., **5**, 577, (1912); Chem. Zentralb., **1912**, II, 456. A glass flask with neck inserted tangentially is described.

† Z. öff. Chem., **19**, 447 (1913).

‡ Z. öff Chem., **19**, 447 (1913).

§ The value given by Lewkowitsch for the acetyl value of the wax alcohols, namely 99 to 103, seems to be an error, as the theoretical value for myricyl alcohol is 116.7 and that of ceryl alcohol is 128.1.

waxes the values were 45.9 and 47.6 per cent of alcohols and 5 and 3 per cent of hydrocarbons.

5. Colophony can be qualitatively detected in the extract made with 70 per cent alcohol by the Morawski reaction (quantitative determination, see page 471).

VII. Montan Wax

(*a*) **General.** In lignite (brown coal) is found a variable amount of bitumen* (from 3 to 30 per cent). When the lignite is extracted with naphtha or benzol the bitumen is obtained in the form of montan wax; if the lignite is destructively distilled, the bitumen yields lignite-tar. The value of a coal for extraction and for distillation depends on the kind of material available and the local conditions. Eight per cent of bitumen, calculated to dry coal and with usual methods of extraction represents the lower limit that can be profitably worked; at times 30 per cent has been obtained. The method of extraction is important; the method described on page 107 is used in the laboratory. Benzol extracts more bitumen than does naphtha, but even in lignite from which 50 per cent of the moisture has been removed, benzol does not extract all the bituminous material of which 40 to 50, at times 70 per cent remains† behind in the coal; this may be obtained subsequent to the extraction by destructive distillation. By using a mixture of benzol and alcohol for the extraction, this dissolving the superficial covering of water, it is claimed that the yield of bitumen may be increased 50 per cent beyond that possible with benzol alone. By using benzol under high pressure (6 atmospheres) and at high temperature (260°) an almost quantitative extraction is possible (the yield being raised from 11 to 25 per cent). In considering the industrial worth of a process it must be remembered that the completely extracted lignite must be mixed with larger amounts of binding material to make it able to compete as briquettes with bituminous coal. Lignite has a fuel value of 2450 to 2550 calories, briquettes of from 4800 to 5200 calories, and bituminous coal about 7000 calories.

Formerly‡ lignite was treated with steam (or moist coal from the mine with superheated steam) but the present procedure is to extract the dried lignite with benzol. Molten naphthalene has been suggested as the solvent.

* Chem. Zeitung, **41**, 129, 150 (1917).

† Braunkohle, **3**, 99 (1904); **15**, 235 (1916). D. R. P. 305 349. Ber., **49**, 1465 (1916).

‡ D. R. P. 2232; also 101373; also 204256

The crude montan wax is purified by distillation with superheated steam in a vacuum.* The montan wax is used for the preparation of shoe polish, phonograph records, insulating material for cables, floor wax, and composition greases, and to a small extent in the candle industry.

The origin of the montan wax is uncertain.† It has been thought that the material was produced by certain algae. Others have supposed that it originated from the resins of coniferous and deciduous trees; but the comparison of montan wax with retinit, a fossil resin found in deposits of lignite, does not lend probability to this view. The fatty and waxy components of plants have been considered by some investigators as the possible source. The occurrence of both waxy and resinous material in montan wax has led others to believe the montan wax to be derived from such substances.

(*b*) **Properties.** Montan wax from Saxon-Thuringian lignite is dark, hard, with conchoidal fracture, and melting point 80 to 90°; Silesian wax melts at 56°, Bohemian is a thick syrup; bitumen from Lausitz is more resinous having a melting point from 115 to 120°. Montan wax‡ has a density of about 1; saponification value, from 60 to 80; an acid value, 20 to 30; iodine value, 12 to 19; flash point, 300°; a calorific value of about 9700 calories.

Montan wax (like beeswax) is not completely saponifiable with alcoholic potash under the usual conditions, so xylol and 2-normal alkali is used (page 523). The crude wax gives the Liebermann test for cholesterin (page 519). The portion crystallizing from alcohol has at 50° a rotatory power of + 10°; the benzol-soluble portion of the unsaponifiable material, because of its high content of resin, had a rotatory power of + 56.5°.

Crude montan wax§ contains, besides sulphur derivatives and difficultly characterizable components, a considerable amount of acids (stated by various observers to range from 50 to 90 per cent) and unsaponifiable material. The acids, melting from 73 to 86°, are said to be a mixture of arachidic, behenic and lignoceric acids. They are brown, have an acid value 84; saponification value, 122; iodine value 6.7; average molecular weight, 460. The difference between acid and

* Z. angewandte Chem., **14**, 1110 (1901); D. R. P. 237 012

† Braunkohle, **3**, 98 (1904); Berichte, **35**, 1212 (1902).

‡ Braunkohle, **6**, 218 (1907); Chemiker Zeitung, **30**, 1167 (1906); Ber., **35**, 1216 (1902).

§ Braunkohle, **6**, 220 (1907). Monatshefte, **34**, 1143 (1913). Z. angew. Chem., **13**, 556 (1900). Chem. Umschau, **16**, 211 (1909): **23**, 57 (1916). J. Chem. Soc., **99**, 2298 (1911). Ber., **49**, 1469 (1916); **35**, 1215 (1902).

saponification value is due to the presence of anhydrides or lactones. A montanic acid of composition $C_{29}H_{58}O_2$ (M. P., 83 to 84°) and an iso-acid $C_{28}H_{56}O_2$ (M. P., 86°) have been identified.

The unsaponifiable matter may be an alcohol, or a ketone, or an ester; it (36 per cent of the crude wax) is brown, wax-like, brittle; with melting point 68 to 71°, specific gravity greater than 1; refractive index at 100°, 1.476; iodine value, 22; acetyl value, 118. It gives the Liebermann test for cholesterin. Saturated aliphatic alcohols of molecular weight 356 are probably present; resinous alcohols, sterines and small amounts of hydrocarbons are also suspected to be present.

The montan resin extracted with 96 per cent alcohol amounts to about 21 per cent of the wax; it is brown, of melting point from 72 to 75°, acid value about 43, saponification value 73, iodine value 23 and density greater than 1. Industrially the resin is extracted from the montan wax by benzol or toluol; the wax separates on cooling the solution, the resin is in solution in the benzol.

The resin may also be obtained by treatment of the montan wax with liquid sulphur dioxide, in which the unsaturated resins are easily soluble, the saturated components of the wax being insoluble.

On distilling crude montan wax there is obtained a tallow-like non-crystalline mass of melting point 55 to 60°. By repeated distillation, more oily material is obtained, and little paraffin; the latter is said to be docosane of melting point 52 to 53°. When distilled under atmospheric pressure, carbon monoxide and dioxide, hydrogen sulphide, methane, and olefins are evolved and a partially liquid mass of petroleum-like hydrocarbons is obtained. Distilling in a vacuum gives a yellowish-white waxy material of melting point 74 to 78°; a pitch may be obtained, this containing free acid. lactones, ketones, asphaltic material, and unchanged wax.

By distillation of the montan wax with steam in a partial vacuum (and repeated pressing of the distillate after extraction with naphtha and decolorization with bone-black), there is obtained a white, crystalline mass of melting point 70 to 80°. The constants of the purified material are given in Table 121. The acid is montanic acid; the unsaponifiable material is montanic acid ketone.

(*c*) **Tests.** The material is examined for mechanical impurities, melting point and other properties which may be useful. In saponifying as already pointed out, xylol and 2-normal alkali are used. Heating to 100° causes decomposition with liberation of carbon dioxide and water, the acid value dropping from 84 to 54, the saponification value from 122 to 115. The method of Spitz and Hönig using naphtha

TABLE 121

PROPERTIES OF DISTILLED AND REFINED MONTAN WAX

	Lewkowitsch	Graefe			Eisenreich	Marcusson and Smelkers
Melting point	80	80	77	75	77	73 to 75
Acid value	123	102	71	42	93	65
Ester value	4	. .	3	20	2	11
Saponification value	127	102	74	62	95	76
Iodine value	.. ..	10	. ..	....	12	....
Calculated content of Montanic acid	93	77	54	32	70	50
Unsaponifiable	7	23	46	68	30	50

or benzol gives non-separating emulsions. The separation of acids and unsaponifiable matter is easily accomplished by precipitating the acids with $CaCl_2$ after saponification; the dry calcium salts are extracted with acetone.

CHAPTER IX

PHYSICO-CHEMICAL TABLES

I. Thermometer Corrections

For the lower temperature of the protruding thread of mercury.

By direct experiment*.

The corrections are for thermometers of Jena or Weber-Friedrichs glass.

n = length of protruding thread in thermometer degrees.

$t - t^{\circ}$ = difference in the observed temperature of the thread and of the surrounding air; this latter is to be determined with a thermometer protected from the heat. It is supported with its bulb at the height of half the length of protruding thread at a distance of 1 decimeter from the main thermometer.

The corrections in the table are to be added to the observed reading of the main thermometer.

TABLE 121

Thermometer with inclosed scale (0 to 360°). Length of degrees 0.9 to 1.1 mm.

$t - t^{0}$	70	80	90	100	110	120	130	140	150	160	170	180	190	200	210	220	$t - t^{0}$
n = 10	0	0	0.05	0.05	0.05	0.05	0.1	0.1	0.1	0.15	0.15	0.15	0.2	0.2	0.2	0.2	10 = n
20	0.1	0.1	0.15	0.2	0.25	0.25	0.25	0.3	0.3	0.3	0.35	0.4	0.45	0.5	0.5	0.55	20
30	0.25	0.3	0.3	0.35	0.4	0.4	0.45	0.5	0.5	0.55	0.6	0.65	0.75	0.8	0.8	0.85	30
40	0.3	0.35	0.4	0.5	0.55	0.6	0.65	0.65	0.7	0.75	0.85	0.9	1.0	1.1	1.1	1.2	40
50	0.4	0.45	0.5	0.6	0.7	0.8	0.85	0.9	0.9	1.0	1.0	1.2	1.3	1.4	1.4	1.5	50
60	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.1	1.1	1.2	1.3	1.5	1.6	1.7	1.8	1.9	60
70	0.65	0.75	0.85	1.0	1.1	1.2	1.3	1.3	1.4	1.4	1.6	1.7	1.8	2.0	2.1	2.2	70
80	0.75	0.85	1.0	1.1	1.3	1.4	1.5	1.5	1.6	1.7	1.8	2.0	2.1	2.3	2.4	2.5	80
90	0.85	1.0	1.1	1.3	1.4	1.6	1.7	1.8	1.9	1.9	2.1	2.2	2.4	2.6	2.7	2.9	90
100	1.0	1.1	1.3	1.5	1.6	1.8	2.0	2.0	2.1	2.2	2.4	2.5	2.7	2.9	3.1	3.2	100
110	....	....		1.7	1.9	2.0	2.2	2.3	2.3	2.4	2.6	2.8	3.0	3.2	3.4	3.6	110
120				1.9	2.1	2.3	2.4	2.5	2.5	2.7	2.9	3.1	3.4	3.6	3.8	4.0	120
130					2.3	2.5	2.7	2.7	2.8	2.9	3.2	3.4	3.7	3.9	4.1	4.3	130
140					2.5	2.7	2.9	3.0	3.0	3.2	3.5	3.7	4.0	4.2	4.5	4.7	140
150								3.2	3.3	3.5	3.8	4.1	4.3	4.6	4.8	5.1	150
160								3.3	3.6	3.8	4.1	4.3	4.6	4.9	5.2	5.4	160
170									3.8	4.1	4.4	4.7	5.0	5.3	5.5	5.8	170
180									4.1	4.4	4.7	5.0	5.3	5.6	5.9	6.2	180
190												5.3	5.7	6.0	6.3	6.6	190
200												5.7	6.0	6.3	6.7	7.0	200
210													6.3	6.7	7.0	7.4	210
220													6.6	7.0	7.4	7.8	220

* Rimbach, Zeit. f. Instrumentenkunde 10, 135 (1890).

TABLE 122

Thermometer with scale on stem (0 to 360°). Length of degrees 1 to 1 6 mm.

$t - t^0$	70	80	90	100	110	120	130	140	150	160	170	180	190	200	210	220	$t - t^0$
n = 10	0	0 05	0 05	0 05	0 1	0 1	0 1	0 15	0 2	0 2	0 2	0 25	0 3	0 35	0 35	0 4	10 = n
20	0 15	0 15	0 2	0 2	0 25	0 3	0 3	0 4	0 45	0 45	0 5	0 55	0 55	0 6	0 65	0 65	20
30	0 25	0 3	0 35	0 4	0 45	0 5	0 55	0 6	0 65	0 7	0 75	0 8	0 85	0 9	0 95	0.95	30
40	0 35	0 4	0 5	0 55	0 6	0 7	0 75	0 8	0 9	0 95	0 1	1 0	1 1	1 2	1 2	1 3	40
50	0 45	0 55	0 6	0 7	0 8	0 9	0 95	1 0	1 1	1 2	1 2	1 3	1 4	1 4	1 5	1 6	50
60	0 55	0 65	0 75	0 9	1 0	1 1	1 2	1 2	1 3	1 4	1 5	1 6	1 7	1 7	1 8	1 9	60
70	0 7	0 8	0 9	1 1	1 2	1 3	1 4	1 5	1 6	1 7	1 8	1 9	1 9	2 0	2 1	2 2	70
80	0 8	0 9	1 0	1 2	1 4	1 5	1 6	1 7	1 8	1 9	2 0	2 1	2 2	2 3	2 4	2 5	80
90	0 9	1.0	1 2	1 4	1 6	1 7	1 9	2 0	2 1	2 2	2 3	2 4	2 5	2 6	2 8	2 9	90
100	1 0	1 2	1 3	1 6	1 8	2 0	2 1	2 2	2 3	2 4	2 6	2 7	2 8	2 9	3 1	3 2	100
110				1 8	2 0	2 2	2 3	2 4	2 5	2 7	2 8	3 0	3 1	3 3	3 4	3 6	110
120				2 0	2 2	2 4	2 6	2 7	2 8	2 9	3 1	3 3	3 4	3 6	3 7	3 9	120
130					2 4	2 7	2 8	2 9	3 0	3 2	3 4	3 6	3 7	3 9	4 1	4 3	130
140					2 7	2 9	3 1	3 2	3 3	3 5	3 7	3 9	4 0	4 2	4 4	4 6	140
150									3 5	3 7	4 0	4 1	4 3	4 6	4 8	5 0	150
160									3 7	4 0	4 2	4 5	4 7	4 9	5 1	5 4	160
170									4 0	4 3	4 5	4 8	5 0	5 2	5 5	5 8	170
180									4 3	4 5	4 8	5 1	5 3	5 6	5 9	6 1	180
190												5 4	5 6	5 9	6 2	6 5	190
200												5 7	6 0	6 3	6 6	6 9	200
210													6 3	6 7	7 0	7 3	210
220													6 7	7 0	7 4	7 7	220

TABLE 123

Normal (inclosed scale and stem) thermometers, 0 to 100° with 0 1 degree divisions. Length of degrees about 4 mm.

$t - t^0$	30	35	40	45	50	55	60	65	70	75	80	85	$t - t^0$
n = 10	0 05	0 05	0 05	0 05	0 05	0 05	0 05	0 05	0 1	0 1	0 1	0 1	10 = n
20	0 1	0 1	0 15	0 15	0 15	0 15	0 15	0 2	0 2	0 2	0 2	0 25	20
30	0 2	0 2	0 25	0 25	0 25	0 25	0 25	0 25	0 3	0 35	0 35	0 35	30
40	0 3	0 2	0 3	0 35	0 35	0 35	0 4	0 4	0 45	0 45	0 5	0 5	40
50	0 35	0 3	0 4	0 4	0 45	0 45	0 5	0 5	0 55	0 55	0 6	0 65	50
60	0 45	0 5	0 5	0 55	0 55	0 55	0 6	0 65	0 65	0 7	0 75	0 8	60
70						0 65	0 7	0 7	0 75	0 8	0 85	0 9	70
80							0 75	0 8	0 85	0 95	1 0	1 1	80
90								0 9	1 0	1 1	1 1	1 2	90
100									1 1	1 2	1 3	1 3	100

II. Reduction of Weight to Vacuum*

TABLE 124

To the weight in air P is added the correction

$$P\delta\left(\frac{1}{d} - \frac{1}{d_1}\right),$$

where

d = specific gravity of the substance weighed,
d_1 = specific gravity of the weights,
δ = density (weight of 1 c.c. in grams) of air during the weighing (approximately $\delta = 0.0012$).

In the following table $R = 1000\,\delta\left(\frac{1}{d} - \frac{1}{d_1}\right)$ for bodies having a specific gravity between 0.70 and 1.35, using either platinum-iridium weights ($d_1 = 21.55$) or brass weights ($d_1 = 8.4$). The weight in a vacuum is therefore $P + \frac{PR}{1000}$.

d	R platinum-iridium weights	R brass weights	d	R platinum-iridium weights	R brass weights
0.70	+1.66	+1.57	0.96	+1.20	+1.10
0.72	1.62	1.52	0.98	1.17	1.08
0.74	1.57	1.48	1.00	1.14	1.06
0.76	1.53	1.44	1.02	1.12	1.03
0.78	1.48	1.40	1.04	1.10	1.01
0.80	1.44	1.36	1.06	1 08	0.99
0.82	1.41	1.32	1.08	1.06	0.97
0.84	1.38	1.28	1.10	1 04	0.95
0.86	1.34	1.25	1.15	0.99	0.90
0.88	1.31	1.22	1.20	0.94	0.86
0.90	1.28	1.19	1.25	0 90	0.82
0.92	1.25	1.16	1.30	0.87	0.78
0.94	1.22	1.13	1.35	0.84	0.74

* Landolt-Börnstein-Roth, 15.

III. Density of Water*

TABLE 125

Between 10 and 25° (Hydrogen Scale)

Degree	One-tenth degrees 0	1	2	3	4	5	6	7	8	9
10	0.999 727	718	709	700	691	681	672	662	652	642
11	632	622	612	601	591	580	569	558	547	536
12	525	513	502	490	478	466	454	442	429	417
13	404	391	379	366	353	339	326	312	299	285
14	271	257	243	229	215	200	186	171	156	141
15	126	111	096	081	065	050	034	018	002	*986
16	0.998 970	953	937	920	904	887	870	853	836	819
17	801	784	766	749	731	713	695	677	659	640
18	622	603	585	566	547	528	509	490	471	451
19	432	412	392	372	352	332	312	292	271	251
20	230	210	189	168	147	126	105	083	062	040
21	019	*997	*975	*953	*931	*909	*887	*864	*842	*819
22	0.997 797	774	751	728	705	682	659	635	612	588
23	565	541	517	493	469	445	421	396	372	347
24	323	298	273	248	223	198	173	147	122	096
25	071	045	019	*994	*968	*941	*915	*889	*863	*836

* Referred to water of 4° as unity, Landolt-Börnstein-Roth, 42

IV. Volume and Weight Per Cent of Aqueous Alcohol*

TABLE 126

v/o = volume per cent. *g/o* = weight per cent

v/o	*g/o*	*v/o*	*g/o*	*v/o*	*g/o*	*v/o*	*g/o*	*v/o*	*g/o*
0	0.00	**21**	17.10	**42**	35.16	**63**	55.17	**84**	78.22
1	0.81	**22**	17.94	**43**	36.05	**64**	56.19	**85**	79.43
2	1.62	**23**	18.78	**44**	36.95	**65**	57.21	**86**	80.65
3	2.42	**24**	19.61	**45**	37.86	**66**	58.24	**87**	81.88
4	3.22	**25**	20.45	**46**	38.77	**67**	59.28	**88**	83.13
5	4.02	**26**	21.29	**47**	39.69	**68**	60.32	**89**	84.39
6	4.83	**27**	22.13	**48**	40.61	**69**	61.37	**90**	85.67
7	5.63	**28**	22.98	**49**	41.54	**70**	62.43	**91**	86.97
8	6.44	**29**	23.83	**50**	42.48	**71**	63.50	**92**	88.30
9	7.25	**30**	24.69	**51**	43.42	**72**	64.58	**93**	89.65
10	8.06	**31**	25.54	**52**	44.37	**73**	65.67	**94**	91.02
11	8.87	**32**	26.40	**53**	45.32	**74**	66.76	**95**	92.42
12	9.68	**33**	27.26	**54**	46.28	**75**	67.86	**96**	93.85
13	10.49	**34**	28.12	**55**	47.24	**76**	68.97	**97**	95.31
14	11.31	**35**	28.98	**56**	48.21	**77**	70.09	**98**	96.82
15	12.13	**36**	29.86	**57**	49.18	**78**	71.22	**99**	98.38
16	12.95	**37**	30.73	**58**	50.16	**79**	72.37	**100**	100.00
17	13.78	**38**	31.61	**59**	51.15	**80**	73.52		
18	14.61	**39**	32.49	**60**	52.15	**81**	74.68		
19	15.44	**40**	33.37	**61**	53.15	**82**	75.85		
20	16.27	**41**	34.26	**62**	54.16	**83**	77.03		

* Landolt-Börnstein-Roth, 305.

V. Density of Mixtures of Alcohol and Water (d 15/4) According to the Per Cent by Weight*

TABLE 127

g = substance in 100 gms. solution. Calculated by the Kaiserl. Normal-Eichungskommission from the experiments of Mendeléjeff. (g/o = weight per cent)

g/o	d 15/4	g/o	d 15/4	g/o	d 15/4	g/o	d 15/4	g/o	d 15/4
1	0 99725	21	0 96956	41	0 93692	61	0.89296	81	0.84533
2	0 99544	22	0 96829	42	0 93489	62	0 89064	82	0 84285
3	0.99368	23	0 96699	43	0.93284	63	0 88832	83	0.84035
4	0.99198	24	0 96566	44	0 93076	64	0.88599	84	0 83784
5	0 99034	25	0 96429	45	0.92866	65	0 88366	85	0 83532
6	0.98877	26	0.96290	46	0 92654	66	0.88132	86	0.83277
7	0.98726	27	0 96145	47	0 92439	67	0 87898	87	0.83019
8	0.98581	28	0 95997	48	0 92223	68	0 87662	88	0 82760
9	0 98443	29	0 95844	49	0 92005	69	0 87426	89	0.82497
10	0.98308	30	0 95687	50	0.91785	70	0 87189	90	0 82233
11	0.98177	31	0 95525	51	0.91565	71	0.86952	91	0 81965
12	0 98050	32	0 95360	52	0 91342	72	0.86714	92	0 81692
13	0.97925	33	0 95190	53	0 91118	73	0.86475	93	0.81417
14	0.97803	34	0 95016	54	0 90893	74	0.86235	94	0 81137
15	0.97683	35	0 94838	55	0 90667	75	0 85995	95	0.80853
16	0.97563	36	0 94656	56	0.90441	76	0 85754	96	0.80564
17	0.97443	37	0.94470	57	0 90214	77	0 85512	97	0.80269
18	0.97324	38	0 94281	58	0.89985	78	0.85268	98	0.79971
19	0.97203	39	0.94087	59	0.89756	79	0.85024	99	0.79666
20	0.97080	40	0 93891	60	0.89526	80	0 84779	100	0.79356

* Landolt-Börnstein-Roth, 301.

VI. Expansion of Mixtures of Ethyl Alcohol and Water*

TABLE 128

(g/o = weight per cent)

g/o	d 0/15 †	d 10/15	d 15/15	d 20/15	d 30/15
0	1.00072	1.00058	1.00000	0.99912	0.99663
1	0.99875	0.99866	0.99812	0 99724	0.99481
2	0.99690	0.99682	0.99630	0 99543	0.99302
3	0.99514	0.99507	0 99454	0.99367	0 99128
4	0.99350	0.99340	0 99284	0.99198	0.98957
5	0.99196	0.99179	0.99120	0.99034	0 98789
0	0.98558	0.98478	0 98393	0.98283	0.97994
5	0.98074	0.97896	0.97768	0.97618	0.97249
20	0 97638	0 97346	0 97164	0.96962	0 96500
25	0.97158	0 96749	0.96513	0 96255	0.95697
30	0.96572	0 96054	0.95770	0.95464	0.94822
35	0.95848	0.95243	0.94920	0.94579	0 93871
40	0.94999	0 94324	0.93973	0.93605	0.92851
45	0.94044	0.93319	0 92947	0.92565	0.91783
50	0 93009	0.92254	0.91865	0 91473	0.90670
55	0.91916	0 91145	0.90746	0.90344	0.89524
60	0.90794	0.90007	0.89604	0.89193	0.88355
65	0.89659	0.88853	0.88443	0.88023	0.87168
70	0.88504	0.87685	0.87265	0.86838	0.85967
75	0.87326	0.86497	0.86070	0.85637	0.84751
80	0.86119	0 85285	0.84852	0.84413	0.83517
85	0.84879	0.84039	0.83604	0 83164	0.82263
90	0.83579	0.82737	0.82304	0.81867	0.80972
95	0.82185	0.81349	0.80923	0.80494	0.79619
96	0.81892	0.81058	0.80634	0 80207	0.79338
97	0.81594	0.80762	0.80339	0.79914	0.79052
98	0.81291	0.80460	0.80040	0.79617	0.78762
99	0.80982	0.80153	0.79735	0.79315	0.78468
100	0.80667	0.79840	0.79425	0.79008	0.78169

* Landolt-Börnstein-Roth, 303.

† To be recalculated to water at 4° by the factor 0.99913.

VII. Densities of Acids and Alkalies

TABLE 129

Potassium Hydroxide at 15° (Lunge)

Specific Gravity	Baumé	Twaddell	100 parts by weight contain		One cubic meter contains (kilograms)	
			K_2O	KOH	K_2O	KOH
1.007	1	1.4	0.7	0.9	7	9
1.014	2	2.8	1.4	1.7	14	17
1.022	3	4.4	2.2	2.6	22	26
1.029	4	5.8	2.9	3.5	30	36
1.037	5	7.4	3.8	4.5	39	46
1.045	6	9.0	4.7	5.6	49	58
1.052	7	10.4	5.4	6.4	57	67
1.060	8	12.0	6.2	7.4	66	78
1.067	9	13.4	6.9	8.2	74	88
1.075	10	15.0	7.7	9.2	83	99
1.083	11	16.6	8.5	10.1	92	100
1.091	12	18.2	9.2	10.9	100	119
1.100	13	20.0	10.1	12.0	111	132
1.108	14	21.6	10.8	12.9	119	143
1.116	15	23.2	11.6	13.8	129	153
1.125	16	25.0	12.4	14.8	140	167
1.134	17	26.8	13.2	15.7	150	178
1.142	18	28.4	13.9	16.5	159	188
1.152	19	30.4	14.8	17.6	170	203
1.162	20	32.4	15.6	18.6	181	216
1.171	21	34.2	16.4	19.5	192	228
1.180	22	36.0	17.2	20.5	203	242
1.190	23	38.0	18.0	21.4	214	255
1.200	24	40.0	18.8	22.4	226	269
1.210	25	42.0	19.6	23.3	237	282
1.220	26	44.0	20.3	24.2	248	295
1.231	27	46.2	21.1	25.1	260	309
1.241	28	48.2	21.9	26.1	272	324
1.252	29	50.4	22.7	27.0	284	338
1.263	30	52.6	23.5	28.0	297	353
1.274	31	53.8	24.2	28.9	308	368
1.285	32	57.0	25.0	29.8	321	385
1.297	33	59.4	25.8	30.7	335	398
1.308	34	61.6	26.7	31.8	349	416
1.320	35	64.0	27.5	32.7	363	432
1.332	36	66.4	28.3	33.7	377	449
1.345	37	69.0	29.3	34.9	394	469
1.357	38	71.4	30.2	35.9	410	487
1.370	39	74.0	31.0	36.9	425	506
1.383	40	76.6	31.8	37.8	440	522
1.397	41	79.4	32.7	38.9	457	543
1.410	42	82.0	33.5	39.9	472	563
1.424	43	84.8	34.4	40.9	490	582
1.438	44	87.6	35.4	42.1	509	605
1.453	45	90.6	36.5	43.4	530	631
1.468	46	93.6	37.5	44.6	549	655
1.483	47	96.6	38.5	45.8	571	679
1.498	48	99.6	39.6	47.1	593	706
1.514	49	102.8	40.6	48.3	615	731
1.530	50	106.0	41.5	49.4	635	756
1.546	51	109.2	42.5	50.6	655	779
1.563	52	112.6	43.6	51.9	681	811
1.580	53	116.0	44.7	53.2	706	840
1.597	54	119.4	45.8	54.5	731	870
1.615	55	123.0	47.0	55.9	754	902
1.634	56	126.8	48.3	57.5	789	940

TABLE 130

Sodium Hydroxide at 15° (Lunge)

Specific Gravity	Baumé	Twaddell	Percent Na_2O	Percent NaOH	One cubic meter contains Na_2O	One cubic meter contains NaOH
1.007	1	1.4	0.46	0.59	4.6	6.0
1.014	2	2.8	0.93	1.20	9.4	12.0
1.022	3	4.4	1.43	1.85	14.6	18.9
1.029	4	5.8	1.94	2.50	20.0	25.7
1.036	5	7.2	2.44	3.15	25.3	32.6
1.045	6	9.0	2.94	3.79	30.7	39.6
1.052	7	10.4	3.49	4.50	36.7	47.3
1.060	8	12.0	4.03	5.20	42.7	55.0
1.067	9	13.4	4.54	5.86	48.4	62.5
1.075	10	15.0	5.10	6.58	54.8	70.7
1.083	11	16.6	5.66	7.30	61.3	79.1
1.091	12	18.2	6.25	8.07	68.3	88.0
1.100	13	20.0	6.81	8.78	74.9	96.6
1.108	14	21.6	7.36	9.50	81.5	105.3
1.116	15	23.2	7.98	10.30	89.0	114.9
1.125	16	25.0	8.57	11.06	96.4	124.4
1.134	17	26.8	9.22	11.90	104.6	134.9
1.142	18	28.4	9.84	12.69	112.5	145.0
1.152	19	30.4	10.46	13.50	120.5	155.5
1.162	20	32.4	11.12	14.35	129.2	166.7
1.171	21	34.2	11.74	15.15	137.5	177.4
1.180	22	36.0	12.40	16.00	146.3	188.8
1.190	23	38.0	13.11	16.91	156.0	201.2
1.200	24	40.0	13.80	17.81	165.6	213.7
1.210	25	42.0	14.50	18.71	175.5	226.4
1.220	26	44.0	15.23	19.65	185.8	239.7
1.231	27	46.2	15.97	20.60	196.6	253.6
1.241	28	48.2	16.70	21.55	207.2	267.4
1.252	29	50.4	17.43	22.50	218.2	281.7
1.263	30	52.6	18.21	23.50	230.0	296.8
1.274	31	54.8	18.97	24.48	241.7	311.9
1.285	32	57.0	19.77	25.50	254.0	327.7
1.297	33	59.4	20.60	26.58	267.2	344.7
1.308	34	61.6	21.43	27.65	280.0	361.7
1.320	35	64.0	22.35	28.83	295.0	380.6
1.332	36	66.4	23.25	30.00	309.7	399.6
1.345	37	69.0	24.18	31.20	325.2	419.6
1.357	38	71.4	25.19	32.50	341.8	441.0
1.370	39	74.0	26.14	33.73	358.1	462.1
1.383	40	76.6	27.13	35.00	375.2	484.1
1.397	41	79.4	28.18	36.36	393.7	507.9
1.410	42	82.0	29.18	37.65	411.4	530.9
1.424	43	84.8	30.27	39.06	431.0	556.2
1.438	44	87.6	31.37	40.47	451.1	582.0
1.453	45	90.6	32.57	42.02	473.2	610.6
1.468	46	93.6	33.77	43.58	495.7	639.8
1.483	47	96.6	35.00	45.16	519.1	669.7
1.498	48	99.6	36.22	46.73	542.6	700.0
1.514	49	102.8	37.52	48.41	568.1	732.9
1.530	50	106.0	38.83	50.10	594.1	766.5

TABLE 131

Specific Gravities of Solutions of Hydrochloric Acid (Lunge and Marchlewski)

Specific Gravity at $\frac{15°}{4°}$ (reduced to vacuum)	Baumé	Twaddell	Weight of HCl in 100 parts by weight of acid	One liter contains (Kilograms) of HCl
1.000	0 0	0.0	0.16	0 0016
1.005	0 7	1	1.15	0.012
1.010	1 4	2	2 14	0 022
1.015	2.1	3	3.12	0 032
1.020	2.7	4	4.13	0 042
1.025	3 4	5	5 15	0 053
1 030	4 1	6	6.15	0 064
1.035	4 7	7	7 15	0 074
1.040	5 4	8	8 16	0 085
1 045	6.0	9	9 16	0 096
1 050	6 7	10	10.17	0 107
1 055	7 4	11	11 18	0 118
1 060	8 0	12	12 19	0 129
1.065	8 7	13	13.19	0.141
1 070	9.4	14	14.17	0 152
1.075	10 0	15	15.16	0.163
1.080	10 6	16	16 15	0 174
1 085	11.2	17	17.13	0.186
1.090	11.9	18	18.11	0 197
1.095	12.4	19	19 06	0 209
1.100	13.0	20	20 01	0.220
1.105	13.6	21	20 97	0.232
1.110	14 2	22	21 92	0 243
1.115	14 9	23	22 86	0.255
1.120	15.4	24	23.82	0.267
1.125	16 0	25	24.78	0.278
1.130	16 5	26	25.75	0 291
1.135	17.1	27	26 70	0.303
1.140	17 7	28	27.66	0 315
1.1425	18 0		28.14	0.322
1.145	18.3	29	28.61	0 328
1.150	18 8	30	29 57	0 340
1.152	19.0		29.95	0 345
1.155	19.3	31	30.55	0 353
1.160	19.8	32	31.52	0.366
1.163	20.0		32.10	0.373
1.165	20.3	33	32.49	0.379
1.170	20.9	34	33.46	0.392
1.171	21 0		33.65	0.394
1.175	21.4	35	34.42	0.404
1.180	22.0	36	35.39	0.418
1.185	22.5	37	36.31	0.430
1.190	23.0	38	37 23	0.456
1.195	23.5	39	38.16	0.456
1.200	24.0	40	39.11	0.469

VIII. International Atomic Weights, 1922

TABLE 132

	Symbol	Atomic weight
Aluminum	Al	27.0
Antimony	Sb	120.2
Argon	A	39.9
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	209.0
Boron	B	10.9
Bromine	Br	79.92
Cadmium	Cd	112.40
Cæsium	Cs	132.81
Calcium	Ca	40.07
Carbon	C	12.005
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.1
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	70.1
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	4.00
Holmium	Ho	163.5
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.20
Lithium	Li	6.94
Lutecium	Lu	175.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.6
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
Niton (radium emanation)	Nt	222.4
Nitrogen	N	14.008
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.9
Radium	Ra	226.0
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	45.1
Selenium	Se	79.2
Silicon	Si	28.1
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulphur	S	32.06
Tantalum	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.15
Thulium	Tm	169.9
Tin	Sn	118.7
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.2
Vanadium	V	51.0
Xenon	Xe	130.2
Ytterbium (Neoytterbium)	Yb	173.5
Yttrium	Yt	89.33
Zinc	Zn	65.37
Zirconium	Zr	90.6

IX. Heating Liquids*

TABLE 133

Name	Boiling point at 760 mm., °C.	Change of temperature for 1 mm. change of pressure, °C.	German** Prices for 1 kilo (One mark = $0 25)
Methyl formate	31.75	0 034	13.20
Ethyl ether	34.60	0 036	2 20
Ethyl bromide	38 40	0 036	6 60
Carbon bisulphide	46 3	0 042	3 50
Acetone	56 1	0.030	1.90
Chloroform	61.20	0 035	2.70
Methyl alcohol	64.70	0 030	8.50
Carbon tetrachloride	76 75	0 044	4.00
Ethyl acetate	77.15	0 041	3.60
Ethyl alcohol	78 4	0 034	3.15
Benzol	80.2	0 043	3.30
Acetonitrile	81.60	0 030	100.00
Propyl alcohol	97.20	0 038	19.00
Ethyl propionate	99.10	0 040	39.00
Water	100 00	0 0375	
Toluol	110.7	0 042	2.80
Pyridin	115 50	0.044	40.00
Chlorbenzol	132.00	0 049	11.00
m-Xylol	139.2	0 052	15.50
Anisol	153.80	0.048	35 00
Brombenzol	156 15	0.053	19.00
Dimethyl oxalate	163.3	0.047	22.80
Phenol	181 5	0 050	1.00
Anilin	184.40	0 051	4.00
Benzonitril	191.30	0 054	88.00
Acetophenone	201.5	0.060	30.30
Nitrobenzol	210.85	0.048	3.40
Naphthalene	217.7	0 059	1.00
Diphenyl	254.9	0.061	150.00
Diphenylmethan	260.5	0.067	140.50
α-Brom-naphthalene	279.6	0.065	16 00
Phthalic anhydride	284.5	0.068	14.00
Benzophenon	305.4	0.065	90 00
Anthracene	351.0	0.068	200.00
Triphenylmethan	358.0	0.069	200.00
Anthraquinone	380.0	0.075	28.70
Sulphur	444.53	0.082	1.50

* Landolt-Börnstein-Roth, 327.

** Prices before the war.

X. Boiling Point of Water at Different Pressures (Regnault)

TABLE 134

Pressure in millimeters of mercury

B. P.	m. m.	B. P.	m. m.	B. P.	m. m.	B. P.	m. m.	B. P.	m. m.
1.3°	10	66.5°	200	81 7°	380	91.7°	560	98.7°	725.35
22.4	20	67.6	210	82.4	390	92.2	570	98.9	727.96
29.1	30	68 7	220	83.0	400	92 6	580	98.9	730.58
34.2	40	69.7	230	83 6	410	93.1	590	99 0	733.21
38.3	50	70.7	240	84.2	420	93.5	600	99.1	735.85
41.7	60	71.6	250	84 8	430	94.0	610	99.2	738.50
44.6	70	72.5	260	85.4	440	94.4	620	99.3	741.16
47.2	80	73.4	270	86.0	450	94.8	630	99.4	743.83
49.6	90	74.3	280	86 5	460	95.3	640	99.5	746.50
51.7	100	75.1	290	87.1	470	95 7	650	99.6	749.18
53.6	110	75.9	300	87.7	480	96.1	660	99.7	751.87
55.4	120	76 7	310	88.2	490	96.5	670	99.8	754.57
57.2	130	77 5	320	88 7	500	96.9	680	99.9	757.28
58.7	140	78.2	330	89 2	510	97 3	690	100 0	760.00
60.2	150	79.0	340	89 7	520	97.7	700	100.1	762.73
61.6	160	79 7	350	90 2	530	98 1	710	100.2	765.46
63.0	170	80.4	360	90 7	540	98 5	720 15	100.3	768.20
64.2	180	81.0	370	91 2	550	98.6	722.75	100.4	771.95
65.4	190								

INDEX OF AUTHORS

INDEX OF SUBJECTS